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ON THE FORMATION AND GROWTH OF SUB-3 NM
ATMOSPHERIC PARTICLES AND MOLECULAR CLUSTERS

JENNI KONTKANEN

Division of Atmospheric Sciences
Department of Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

Academic dissertation

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Author's Address: Department of Physics
P.O. Box 64
FI-00014 University of Helsinki
jenni.kontkanen@helsinki.fi

Supervisors: Professor Markku Kulmala, Ph.D.
Department of Physics
University of Helsinki

Professor Veli-Matti Kerminen, Ph.D.
Department of Physics
University of Helsinki

Reviewers: Professor Hannele Korhonen, Ph.D.
Finnish Meteorological Institute

Professor Markus Olin, Ph.D.
VTT Technical Research Centre of Finland Ltd

Opponent: Associate Professor Jeffrey Pierce, Ph.D.
Department of Atmospheric Science
Colorado State University

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On the formation and growth of sub-3 nm atmospheric particles and molecular clusters

Jenni Salla Sofia Kontkanen

University of Helsinki, 2016

Abstract

Air consists of different gas molecules but also liquid or solid aerosol particles. Despite their small size, aerosol particles significantly affect human life: they deteriorate air quality and influence the climate directly by scattering and absorbing solar radiation, and indirectly by modifying the properties of clouds. The majority of atmospheric aerosol particles are formed in the process called new particle formation. New particle formation proceeds by the formation of nanometer-sized clusters from low-volatile vapors and their following growth to larger particles. If the particles produced in this process reach large enough sizes they can finally act as cloud condensation nuclei and thus affect the climate.

Due to the climate effects of atmospheric particle formation, it has been widely studied in recent decades. However, because of challenges in detecting nanometer-sized clusters and particles and their precursor vapors, many questions remain open. The aim of this thesis is to elucidate some of the unresolved issues related to the first steps of particle formation and growth by investigating the dynamics of sub-3 nm atmospheric particles and molecular clusters.

The research in this thesis was conducted by analyzing measurements performed with novel instrumentation in different environments in the field and in the laboratory. The primary instrument was the Particle Size Magnifier (PSM), which is a recently developed condensation particle counter able to detect particles down to even 1 nm. The measurements with ion mobility spectrometers measuring atmospheric ions, and chemical ionization mass spectrometers detecting low-volatile gaseous compounds were also utilized. In addition, cluster population simulations were performed.

The concentration of sub-3 nm particles was observed to vary strongly between different environments. The highest concentrations were detected in polluted environments, likely due to anthropogenic sources of precursor vapors. In boreal forest sub-3 nm particle concentration was higher in summer than in winter, suggesting the importance of biogenic precursor vapors. At all the study sites, sub-3 nm particle concentration was higher during day-time than at night. Electrically neutral particles were observed to dominate the sub-3 nm particle population in polluted environments and in boreal forest during spring and summer.

The formation of sub-2 nm molecular clusters and their further growth were found to be two separate processes. Neutral particle formation mechanisms were observed to dominate over ion-mediated mechanisms. The results indicate that sulfuric acid is a key compound in particle formation but low-volatile organic compounds are likely also important, especially in accelerating particle growth. In the system containing only sulfuric acid, base compounds, and ions, small acid–base clusters and ions can also enhance the growth.

The understanding of the first steps of particle formation and growth obtained in this thesis is essential when trying to reduce the uncertainties in the climate predictions related to the indirect effects of aerosol particles. In addition, the knowledge of aerosol formation mechanisms is needed to solve air quality problems faced in polluted environments.

Keywords: atmospheric aerosol particles, molecular clusters, particle formation and growth

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List of publications

This thesis consists of an introductory review, followed by six research articles. In the introductory part, the papers are cited according to their roman numerals. Papers II and V are reprinted with permission from the publisher, and other papers are reproduced under the Creative Commons Attribution 3.0 License.

- I** **Kontkanen, J.**, Lehtipalo, K., Ahonen, L., Kangasluoma, J., Manninen, H. E., Hakala, J., Rose, C., Sellegri, K., Xiao, S., Wang, L., Qi, X., Nie, W., Ding, A., Yu, H., Lee, S., Kerminen, V.-M., Petäjä, T., and Kulmala, M.: A global view on atmospheric concentrations of sub-3 nm particles measured with the Particle Size Magnifier, *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-847, in review, 2016.
- II** Kulmala, M., **Kontkanen, J.**, Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Järvinen, E., Äijälä, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkilä, J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin, R. L., Duplissy, J., Vehkamäki, H., Bäck, J., Kortelainen, A., Riipinen, I., Kurtén, T., Johnston, M. V., Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., and Worsnop, D. R.: Direct observations of atmospheric aerosol nucleation, *Science*, 339, 943–946, doi:10.1126/science.1227385, 2013. Reprinted with permission from AAAS.
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- V** Lehtipalo, K., Rondo, L., **Kontkanen, J.**, Schobesberger, S., Jokinen, T., Sarnela, N., Kürten, A., Ehrhart, S., Franchin, A., Nieminen, T., Riccobono, F., Sipilä, M., Yli-Juuti, T., Duplissy, J., Adamov, A., Ahlm, L., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., Dommen, J., Downard, A. J., Dunne, E. M., Flagan, R. C., Guida, R., Hakala, J., Hansel, A., Jud, W., Kangasluoma, J., Kerminen, V.-M., Keskinen, H., Kim, J., Kirkby, J., Kupc, A., Kupiainen-Määttä, O., Laaksonen, A., Lawler, M. J., Leiminger, M., Mathot, S., Olenius, T., Ortega, I. K., Onnela, A., Petäjä, T., Praplan, A., Rissanen, M. P., Ruuskanen, T., Santos, F. D., Schallhart, S., Schnitzhofer, R., Simon, M., Smith, J. N., Tröstl, J., Tsagkogeorgas, G., Tomé, A., Vaattovaara, P., Vehkamäki, H., Vrtala, A. E., Wagner, P. E., Williamson, C., Wimmer, D., Winkler, P. M., Virtanen, A., Donahue, N. M., Carslaw, K. S., Baltensperger, U., Riipinen, I., Curtius, J., Worsnop, D. R., and Kulmala, M.: The effect of acid–base clustering and ions on the growth of atmospheric nano-particles, *Nat. Commun.*, 7, 11594, doi:10.1038/ncomms11594, 2016.
- VI** **Kontkanen, J.**, Olenius, T., Lehtipalo, K., Vehkamäki, H., Kulmala, M., and Lehtinen, K. E. J.: Growth of atmospheric clusters involving cluster–cluster collisions: comparison of different growth rate methods, *Atmos. Chem. Phys.*, 16, 5545–5560, doi:10.5194/acp-16-5545-2016, 2016.

1 Introduction

Air consists of different gas molecules but also tiny, liquid or solid particles, which are called aerosol particles. Their concentration, size, and composition vary strongly between different environments. In very clean places, such as in the polar regions, there can be only a few aerosol particles in a cubic centimeter of air (Shaw, 1998), whereas in polluted megacities the same volume contains tens of thousands of particles (Wu et al., 2008). The smallest aerosol particles have diameters of some nanometers, and thus contain only a few molecules, and the largest aerosol particles have diameters of tens of micrometers containing trillions of molecules. The composition of aerosol particles varies depending on their origin: particles found in the air in a pine forest are different from particles detected in a polluted urban area.

Aerosol particles have significant impacts on human life on Earth. Exposure to ambient particulate matter has been estimated to be one of the largest risk factors causing premature deaths globally (Lim et al., 2012). High concentrations of aerosol particles observed in urban areas cause heart and respiratory diseases, lung cancer, and strokes (Pope et al., 2002; Brook et al., 2010; Lepeule et al., 2012), and therefore significantly reduce life expectancy (Apte et al., 2015). Aerosol particles also affect the climate. They alter the Earth's radiative balance by scattering and absorbing sunlight (Charlson et al., 2001; Jacobson et al., 2001). In addition, aerosol particles can act as cloud condensation nuclei (CCN) and thus indirectly affect the climate by modifying the properties of clouds (Twomey, 1974; Albrecht, 1989; Lohmann and Feichter, 2005). Overall, aerosol particles are estimated to have a cooling effect on the climate, and thus they can partly counteract the global warming caused by greenhouse gases (Stocker et al., 2013). However, the uncertainties in determining the magnitude of the indirect climate effects of aerosol particles are large.

Atmospheric aerosol particles can originate from various natural and anthropogenic sources. Primary particles are emitted into the atmosphere readily in particulate form, while secondary particles are formed in the atmosphere via gas-to-particle conversion, often called new particle formation (Kulmala et al., 2004a). Atmospheric new particle formation proceeds by the formation of nanometer-sized molecular clusters and their subsequent growth to larger particles (Kulmala et al., 2000; Zhang et al., 2012). If the particles produced in this process are able to reach large enough sizes (~ 50 – 100 nm), they can potentially act as CCN (Dusek et al., 2006; Kerminen et al., 2012 and references therein). New particle formation has been estimated to be the dominant source of atmospheric aerosol particles (Spracklen et al., 2006; Yu et al., 2010) and also significantly contribute to global CCN concentrations (Spracklen et al., 2008; Merikanto et al., 2009; Pierce and Adams, 2009). Therefore, understanding this process is essential, when trying to reduce the uncertainties in the climate predictions related to the indirect aerosol forcing (Wang and Penner, 2009; Kazil et al., 2010; Makkonen et al., 2012).

Although atmospheric new particle formation has been widely studied in recent decades, the detailed mechanisms of this process are still not well understood (Zhang et al., 2012; Kulmala et al., 2014). This is mainly due to challenges in directly measuring the concentration and composition of nanometer-sized molecular clusters and particles as well as the concentrations of different vapors participating in the formation and growth of particles. Until recently, it was possible to detect only aerosol particles larger than 3 nm, unless they were electrically charged (McMurry et al., 2000). However, instrumental development during recent years has enabled to measure the concentration of sub-3 nm neutral particles by using ion mobility spectrometers and different condensation particle counters (CPCs) (Kulmala et al., 2007, 2012; Sipilä et al., 2008; Manninen et al., 2009a). The development of CPCs using diethylene glycol as a condensing vapor has finally made it possible to detect particles down to even ~1 nm (Jiang et al., 2011; Vanhanen et al., 2011; Wimmer et al., 2013), enabling the direct measurement of the first steps of particle formation. In addition, the rapid development of different mass spectrometry techniques has allowed the detection of low-volatile gaseous compounds participating in atmospheric particle formation (Weber et al., 1995; Petäjä et al., 2009; Ehn et al., 2010, 2014; Jokinen et al., 2012).

One of the open questions related to atmospheric particle formation is the existence of electrically neutral sub-3 nm clusters and particles and their importance in aerosol formation (Kulmala et al., 2000). The continuous existence of ion clusters in the atmosphere has been known for decades (Hirsikko et al., 2011 and references therein) and some studies claim that ion-mediated mechanisms govern atmospheric particle formation (Yu and Turco, 2000, 2008; Kazil et al., 2008). The studies utilizing novel aerosol instruments indicate that sub-3 nm neutral particles also exist in the atmosphere, and that neutral pathways likely dominate over ion-mediated particle formation mechanisms (Kulmala et al., 2007; Lehtipalo et al., 2010; Jiang et al., 2011; Rose et al., 2015a). However, it is unclear if these results apply to all kinds of environmental conditions, or if in some environments ions dominate particle formation. Furthermore, due to a limited number of studies and short measurement periods, the concentrations of neutral sub-3 nm particles in different environments and the variation of concentrations on diurnal and seasonal scales remain to be elucidated.

The role of different gaseous compounds in the formation and growth of atmospheric particles has also been under extensive investigation during the last decades. The importance of sulfuric acid in atmospheric particle formation has been established in numerous field and laboratory measurements (e.g. Weber et al., 1995; Kuang et al., 2008; Paasonen et al., 2010; Sipilä et al., 2010). However, there is strong evidence that other compounds besides sulfuric acid and water are also needed to explain particle formation observed in the planetary boundary layer (Kirkby et al., 2011). According to both theoretical and experimental results, base compounds, such as amines or ammonia, efficiently form clusters with sulfuric acid and therefore could take part in atmospheric particle formation (Kurtén et al., 2008; Petäjä et al., 2011; Almeida et al., 2013; Kürten et al., 2014). In addition, oxidized organic compounds with very low volatility are likely candidates for participating in the formation and growth of particles, especially in forested regions (e.g. O'Dowd et al., 2002; Metzger et al., 2010; Riipinen et al., 2012; Schobesberger et al., 2013; Kirkby et al., 2016). Despite recent

advancements in understanding new particle formation in controlled laboratory conditions, the exact chemical and physical processes governing the formation and growth of particles in the ambient atmosphere are still largely unknown.

The research presented in this thesis aims to elucidate the remaining open questions related to the first steps of atmospheric particle formation and growth. More specifically, the main objectives of this thesis are:

- i) To develop and evaluate theoretical methods to study the dynamics of sub-3 nm particles.
- ii) To obtain a comprehensive picture of the concentrations and dynamics of sub-3 nm atmospheric particles in different environments.
- iii) To understand the first steps of atmospheric new particle formation and growth and the role of neutral and charged particles and different gaseous compounds in these processes.

These objectives are fulfilled by analyzing measurements conducted in different environments in the field and in the laboratory using novel measurement techniques. In addition, cluster population simulations were performed to assess the validity of the analysis methods and to increase the understanding of the studied processes.

In Section 2 of the thesis different processes affecting the dynamics of sub-3 nm atmospheric particles are briefly discussed. Section 3 includes the description of instrumentation, data-analysis methods and cluster population simulations utilized in the thesis. In Section 4 and Section 5 atmospheric sub-3 nm particles and the first steps of particle formation and growth are discussed based on literature and the results of this thesis. In Section 6 the articles included in the thesis are briefly reviewed. Finally, Section 7 summarizes the conclusions of this thesis.

2 Dynamics of sub-3 nm atmospheric particles

When studying the dynamics of sub-3 nm atmospheric particles, one needs to consider different physical and chemical processes modifying the concentration, size and composition of these particles and the properties of gaseous compounds facilitating their formation. The most important processes of these, in the viewpoint of this thesis, are summarized below. It should be noted that in the sub-3 nm size range, large gas molecules, molecular clusters and particles can coexist in the atmosphere and it is often not possible to separate them from each other from measurements (Kulmala et al., 2014). Therefore, in the introductory part of this thesis all the objects in the sub-3 nm size range detected with aerosol instruments are in most cases simply referred to as particles.

Chemical reactions in the gas phase are needed for the production of vapors of very low volatility, which are able to form molecular clusters in the atmosphere and condense on existing particles. The most important low-volatile vapor in atmospheric particle formation is thought to be sulfuric acid (e.g. Weber et al., 1995; Sipilä et al., 2010), formed in the oxidation of sulfur dioxide. In addition, the oxidation of volatile organic compounds (VOCs) produces oxidized organic species, often called HOMs (highly oxidized organic compounds; Ehn et al., 2012) which seem to be essential for atmospheric particle formation (e.g. Riipinen et al., 2012; Schobesberger et al., 2013; Ehn et al., 2014). These compounds can be divided according to their volatility to extremely low-volatility organic compounds (ELVOCs), low-volatility organic compounds (LVOCs), semi-volatile organic compounds (SVOCs), and intermediate-volatility organic compounds (IVOCs) (Donahue et al., 2012).

Clustering means the formation of nanometer-sized molecular clusters from low-volatile vapors (Kulmala et al., 2014). The cluster formation can be assisted by compounds which are able to stabilize the clusters, such as gaseous ammonia and amines (Kurtén et al., 2008), organic compounds (Donahue et al., 2013), and air ions (Yu and Turco, 2000). The formed clusters may be electrically neutral or charged. The process where two oppositely charged clusters collide and form a neutral cluster is called ion-ion recombination.

Nucleation is traditionally defined as the formation of a molecular cluster of a critical size at which the cluster more likely grows than evaporates (e.g. Oxtoby et al., 1992; Laaksonen et al., 1995). Thus, nucleation includes an energy barrier that the growing clusters need to overcome. It is also possible that instead of traditional nucleation, atmospheric gas-to-particle conversion occurs by the barrierless clustering of molecules (Kulmala et al., 2014). Nucleation can be divided to homogeneous and heterogeneous nucleation. In homogeneous nucleation a critical cluster is formed directly from the gas phase, while in heterogeneous nucleation the formation of a critical cluster occurs on a pre-existing seed particle, which lowers the energy barrier (Fletcher, 1958). Ion-induced nucleation is a special case of heterogeneous nucleation, in which the seed particle is electrically charged, further decreasing the energy barrier (Raes et al., 1985). The formation of a critical cluster by ion-induced nucleation and ion-ion recombination is called ion-mediated nucleation (Yu and Turco, 2000).

Condensation of vapor molecules on particles enables their growth to larger sizes. Condensational growth is mainly limited by the Kelvin effect: the smaller the particle is, the lower the volatility of the vapor (described by saturation vapor pressure) needs to be so that it can condense on the particle (Thomson, 1871). Therefore, it is possible that freshly-formed clusters need to be activated for the growth by some additional vapor before they can overcome the Kelvin barrier and grow further by condensation. The possible mechanisms for the activation of clusters include heterogeneous nucleation (Winkler et al., 2008a), heterogeneous reactions between clusters and organic vapors (Wang et al., 2010), and nano-Köhler-type process, describing the activation of sulfate clusters by soluble organic vapors (Kulmala et al., 2004b). The presence of electric charge may enhance the condensation process due to the increased collision rate between polar vapor molecules and charged particles (Laakso et al., 2003; Nadykto and Yu, 2003).

Coagulation of nanometer-sized clusters and particles onto pre-existing larger aerosol particles is their main loss mechanism, as the coagulation loss rate is highest for the smallest particles. Therefore, the probability of newly-formed particles to survive to larger sizes is largely determined by the competition between their condensational growth and coagulation loss rate (McMurry and Friedlander, 1979; Kerminen et al., 2001; Pierce and Adams, 2007). On the other hand, self-coagulation, i.e. the collisions of particles with other particles in the same mode, can also grow the particle population to larger sizes (Leppä et al., 2011). The presence of charge can increase the coagulation rate (Hoppel and Frick, 1986).

3 Materials and methods

The main factor limiting the understanding of atmospheric particle formation is the challenges in measuring the concentrations and size distributions of sub-3 nm molecular clusters and particles and the concentrations of low-volatile gaseous compounds. In recent years, the development of instruments for these purposes has been rapid (Kulmala et al., 2012). In this section of the thesis, the latest instrumental development is first briefly discussed, after which the measurement and data-analysis methods used in this thesis are described.

Condensation particle counters (CPCs) have been widely used in measuring the concentrations of atmospheric aerosol particles. The operating principle of a CPC is to expose aerosol particles to a supersaturated vapor, which condenses on particles and thus make them grow to sizes where they can be optically detected. For a long time, the lowest detection limit of CPCs was 3 nm (McMurry et al., 2000), and the development of CPCs in recent decades has largely been aimed at lowering that size. For this, different approaches have been used, including, for example, increasing supersaturation inside the instrument by modifying operating temperatures (Mertes et al., 1995; Wiedensohler et al., 1997; Kangasluoma et al., 2015), minimizing the losses of working fluid and particles (Gamero-Castaño and Fernandez de la Mora, 2000; Sgro and de la Mora, 2004), and separating the homogeneous nucleation mode from activated particles based on pulse height analysis or Mie scattering (Sipilä et al. 2008, 2009; Winkler et al., 2008b). Iida et al. (2009) compared different CPC working fluids and recommended selecting diethylene glycol (DEG) due to its favorable properties. Subsequently, several DEG-based instruments have been developed in recent years (Jiang et al., 2011; Vanhanen et al., 2011; Kuang et al., 2012a; Wimmer et al., 2013), allowing the detection of particles down to ~1 nm in mobility diameter. In this thesis, measurements with the Particle Size Magnifier (PSM; Vanhanen et al., 2011) were utilized. The PSM is the first commercially available DEG-CPC (manufactured by Airmodus Ltd). Three generations of PSMs (A09, A10 and A11) have been launched with small differences in the design and in the secondary CPCs, and all of them were used in this thesis. The operating principle of the PSM is explained in more detail in Section 3.1.1.1.

In addition to different CPC-applications, the concentration and size distribution of sub-3 nm particles can be measured with electrical techniques if particles are electrically charged. For this, ion spectrometers have been used already since the early 20th century (Hirsikko et al., 2011 and references therein). In the modern ion spectrometers, including the Balanced Scanning Mobility Particle Sizer (BSMA; Tammet, 2006) and the Air Ion Spectrometer (AIS; Mirme et al., 2007), charged particles are first size-classified based on their electrical mobility and their concentration is then determined by measuring the current that they carry to an electrometer. The major limitation of these instruments is that they do not provide information on electrically neutral particles. However, the development of the Neutral cluster and Air Ion Spectrometer (NAIS; Manninen et al., 2009a; Mirme and Mirme, 2013) allowed to measure the number size distribution of ions down to 0.8 nm and the total particle size distribution, including neutral particles, down to about 2 nm. The measurement of the

total particle size distribution in the NAIS is enabled by charging the particles with a unipolar corona charger. The more detailed description of the operating principle of NAIS is provided in Section 3.1.1.2. In this thesis, NAIS measurements were mainly utilized to study the contribution of ions to particle concentrations in the sub-3 nm size range. In general, the limitation of electrical techniques to detect sub-3 nm particles is their low sensitivity, while condensational methods are prone to the effects of particle chemical composition and environmental conditions (Kulmala et al., 2012; Kangasluoma et al., 2013, 2014, 2016).

For understanding the first steps of new particle formation, it is also essential to determine the composition of molecules and clusters participating in this process. This can be done by utilizing mass spectrometry techniques, which have evolved very rapidly in recent years. The Chemical Ionization Mass Spectrometer (CIMS) has been used to measure the concentrations of sulfuric acid and hydroxyl radical with low detection limits already for decades (Eisele et al., 1993; Petäjä et al., 2009). The development of the Atmospheric Pressure interface Time-Of-Flight (APi-TOF) mass spectrometer enabled to measure the composition of naturally charged molecules and clusters with very high mass resolution (Junninen et al., 2010; Ehn et al., 2010). Jokinen et al. (2012) combined a chemical ionization inlet with the APi-TOF mass spectrometer, creating a CI-APi-TOF mass spectrometer. With this novel instrument it is possible to detect neutral molecules and clusters, containing, for example, sulfuric acid, amines and highly oxidized organic compounds. In this thesis the CI-APi-TOF was used for these purposes in **Papers II** and **V**. The principle of the CI-APi-TOF is explained in more detail in Section 3.1.1.3.

3.1 Measurements

3.1.1 Instrumentation

3.1.1.1 PSM

In this thesis, the size distributions of sub-3 nm particles were measured with a PSM, which is a dual-stage mixing-type CPC. The supersaturation is created in the mixing region of the PSM by turbulently mixing heated flow saturated with DEG with the colder sample flow. As a result, DEG condenses on the particles in the mixed flow and the particles grow in the growth tube of the PSM until reaching diameters of about 90 nm. After that the particles are sampled into a conventional CPC, where they are grown further by condensation of another vapor (usually butanol) and then counted by an optical detector. The level of supersaturation inside the PSM can be changed by adjusting the mixing ratio of saturated and sample flows, or the temperature difference between them (Vanhanen et al., 2011). The PSM can be operated in a so-called scanning mode, in which the saturator flow rate, and thus also the level of supersaturation, is changed in a continuous manner. Therefore, the cut-off size of the instrument (defined as the size at which 50% of the particles are counted) also changes continuously and the size distribution of particles can be measured (Lehtipalo et al., 2014). Usually, a scanning cycle of 120 steps between saturator flow rates of about 0.1 and 1 liters per minute (lpm) is used, which results in a time resolution of 2 min and the size range from

~1 nm to ~2–3 nm. Alternatively, the PSM can also be operated with a fixed saturator flow rate and thus a constant cut-off size.

To determine the cut-off size of the PSM corresponding to a certain saturator flow rate, the instrument needs to be calibrated. Performing an accurate calibration in the sub-3 nm size range is challenging. The calibrations are generally conducted with electrically charged particles as there are no reference instruments for concentration or size-selection techniques for neutral particles. However, the cut-off size of the PSM for neutral particles with certain settings can be even 0.5 nm higher than the cut-off size for electrically charged particles (Kangasluoma et al., 2016a). On the other hand, the chemical composition of particles can affect the cut-off size even more than the charging state due to solubility effects (Kangasluoma et al., 2016a). As inorganic particles are activated by DEG clearly better than organic particles (Kangasluoma et al., 2014; Kangasluoma et al., 2016a), the combined effect of the charging state and the composition can lead to a significant difference (even more than ± 1 nm) in the cut-off size (Kangasluoma et al., 2016a). For inorganic ions the uncertainty in the cut-off size due to these effects has been estimated to be about ± 0.2 nm (**Paper II**; Lehtipalo et al., 2014). The PSMs used in this thesis were calibrated with ammonium sulfate clusters, tungsten oxide particles, silver particles or tetra-alkyl ammonium halide salts used as mobility standards (Kangasluoma et al., 2014). Except for some of the measurements in **Paper I**, a calibration set-up included a high-resolution Herrmann differential mobility analyzer for size selection and an APi-TOF mass spectrometer for verifying the composition of calibration clusters (Kangasluoma et al., 2014). The PSMs were set so that the background caused by homogenous nucleation was negligible. In **Paper I** in the measurements conducted in Helsinki and Hyytiälä during 2014–2016, an automatic background measurement system was used (Kangasluoma et al., 2016b). Therefore, in these measurements the PSMs could be allowed to have higher background, as it could be subtracted from the measurements afterwards.

To obtain particle size distributions from the scanning PSM data, two different inversion methods were used. In the chamber measurements in **Paper V**, the data were inverted by assuming a step-function like cut-off curve for each saturator flow rate. The concentration in each size bin was then obtained by calculating the difference between the concentrations measured at the saturator flow rates corresponding to the upper and lower limits of the size bin, and correcting that with the average detection efficiency of the size bin (Lehtipalo et al., 2014). In **Papers I–IV**, the Gaussian-shaped kernel functions were used for inverting the data. The kernel functions describe the probability at which a particle of a certain size is measured at a certain saturator flow rate, and they were selected to correspond to the measured activation curves and detection efficiencies (Lehtipalo et al., 2014). The concentration in each size bin was calculated using a non-negative matrix inversion routine for the concentration measured at each saturator flow rate.

In **Paper I** PSM measurements from different study sites were compared. The different PSMs had slightly different cut-off sizes and some of the PSMs were used in the scanning mode while some were operated with a fixed saturator flow rate. To enable the comparison between different measurement sites, the particle concentration between about 1 and 3 nm

was determined for all the sites. For most of the sites this was done by utilizing the difference between the concentration measured with the PSM and another aerosol instrument with a cut-off size of 3 nm, i.e. a DMPS (Differential Mobility Particle Sizer; Aalto et al., 2001) or a SMPS (Scanning Mobility Spectrometer; Wang and Flagan, 1990).

3.1.1.2 NAIS

NAIS is an ion mobility spectrometer which can be used for measuring the size distribution of naturally charged ions as well as the total particle size distribution, also including neutral particles (Manninen et al., 2009a; Mirme and Mirme, 2013). For measuring neutral particles the controlled charging with a unipolar corona charger and the electrical filtering of the charger ions are used. The NAIS includes two differential mobility analyzers, which simultaneously classify positive and negative ions based on their electrical mobility. Each of them contains 21 electrometers measuring the current of size-selected ions. The electrical mobility range measured by the NAIS is $3.2\text{--}0.0013\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, which corresponds to the mobility diameter range of 0.8–42 nm. However, when measuring the total particle size distribution, the lowest detectable size is about 2 nm, as particles smaller than that cannot be distinguished from the charger ions (Asmi et al., 2009; Manninen et al., 2011).

3.1.1.3 CI-API-TOF

The CI-API-TOF mass spectrometer consists of a chemical ionization inlet and an API-TOF mass spectrometer (Jokinen et al., 2012). In the CI-inlet ionization is conducted at ambient pressure by a proton transfer reaction or clustering between reagent ions and the sample molecule. In the measurements utilized in this thesis, nitrate ions (NO_3^-) were used as reagent ions. They were produced by ionizing nitric acid by using an alpha radiator, ^{241}Am (**Paper II**), or a soft x-ray source (**Paper V**). The mass spectrometer part of the instrument measures the mass-to-charge ratio of sample ions with high mass resolution (Junninen et al., 2010). The sampling occurs from atmospheric pressure, after which the sample ions pass through three differentially pumped chambers until arriving at the TOF mass spectrometer with high vacuum (10^{-6} mbar). With the CI-API-TOF it is possible to detect sulfuric acid molecules, clusters containing sulfuric acid, and highly oxidized organic compounds. However, calibration methods, needed for obtaining the absolute concentrations, currently exist only for sulfuric acid molecules.

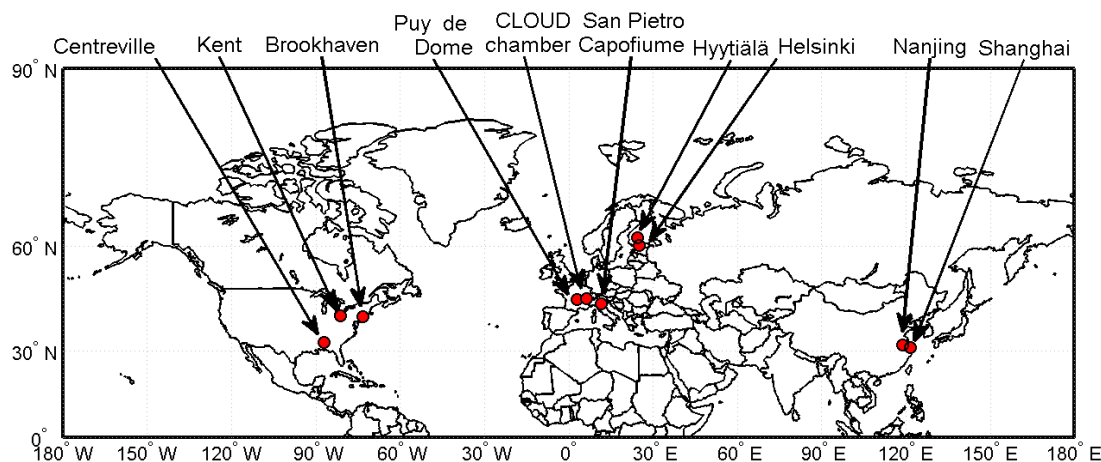


Figure 1. A map showing the locations of the study sites of this thesis (adapted and modified from **Paper I**).

3.1.2 Measurement sites

The measurements in this thesis involve field observations in different environments (**Papers I–IV**) and chamber measurements conducted at the CLOUD (Cosmics Leaving OUtdoors Droplets) facility at CERN (**Paper V**). The locations of measurements sites are shown on a map in Fig. 1.

The measurements at the SMEAR II station (Station for Measuring Forest Ecosystem-Atmosphere Relations; Hari and Kulmala, 2005) were utilized in **Papers I–III**. The station is located in Hyytiälä, southern Finland, about 200 km north of Helsinki Metropolitan area and 50 km north-east of the city of Tampere. The measurement site is surrounded by a rather homogeneous Scots pine forest. The comprehensive measurements of atmosphere-biosphere interactions are conducted continuously at the station, including the measurements of aerosol particles, trace gas concentrations and different meteorological variables. Figure 2 illustrates the time evolution of particle number size distribution measured at the station utilizing different aerosol instruments during spring 2011.

In **Paper IV**, the measurements were performed at the San Pietro Capofiume station in northern Italy (Decesari et al., 2001). The station is surrounded by harvested fields and located about 30 km northeast of the city of Bologna in the Po Valley. The Po Valley region is characterized by high emissions of anthropogenic pollutants originating from power plants and industrial areas.

In **Paper I** data measured at different sites were compared. The sites include the measurement stations in Hyytiälä and San Pietro Capofiume, described above, and seven other measurement sites around the world. These sites include two additional European sites: the

SMEAR III station in the city of Helsinki, southern Finland (Järvi et al., 2009), and the Puy de Dôme station located at the top of a mountain (1465 m above sea level) in central France (Venzac et al., 2009). In the United States, measurements from three different sites were utilized, including a site in Kent, Ohio, a site in Brookhaven, New York (Yu et al., 2014), and a site in Centreville, Alabama (Xu et al., 2015). The measurement sites in Kent and Brookhaven are located within the urban neighborhood while the Centreville site is surrounded by agricultural land and a mixed deciduous forest. In addition, measurements from two Chinese megacities, Shanghai and Nanjing, were utilized (Ding et al., 2013; Xiao et al., 2015). The summary of the field measurements analyzed in this thesis is shown in Table 1.

The CLOUD facilities at CERN allow studying atmospheric particle formation in extremely clean and well-controlled conditions (Kirkby et al., 2011; Duplissy et al., 2016). The CLOUD chamber is a cylindrical, stainless steel reaction chamber with the volume of 26 m³. The chamber is filled with ultrapure synthetic air and the temperature of the chamber can be accurately controlled between 207 K and 310 K. To study ion-mediated particle formation mechanisms, the chamber can be exposed to a pion beam from the CERN Proton Synchrotron, which increases the ion production rate in the chamber. On the other hand, a high voltage clearing field can be applied to remove all the ions from the chamber. The chamber can be irradiated with UV light to trigger the photochemical production of low-volatile vapors. During the experiments, the concentrations of different trace gases, including sulfuric acid, ammonia, amines or organic compounds, can be accurately controlled.

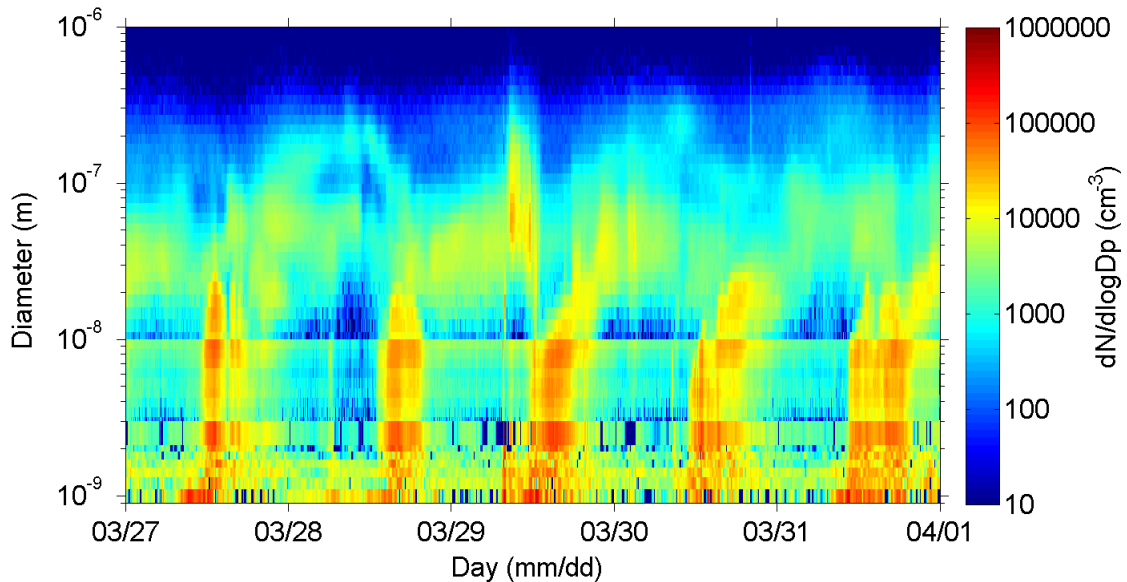


Figure 2. Time evolution of particle number size distribution on a five-day period with particle formation events in Hyytiälä during spring 2011. The particle size distribution from 1 to 3 nm was measured with a PSM, from 3 to 10 nm with a NAIS, and from 10 to 1000 nm with a DMPS (adapted from **Paper II**).

Table 1. A summary of the field measurements of sub-3 nm particle concentrations analyzed in this thesis. In the second column, “proto”, “A09”, “A10”, and “A11” refer to different generations of the PSM. The DMPS and the SMPS are mentioned as the differences between the concentrations measured with them and the concentrations measured with the PSM were utilized.

Measurement site	Instruments	Time period	Size range (nm)
Hyytiälä (HTL 10 aut)	PSM proto*, DMPS, NAIS	4.8–27.8.2010	1.3–3.0
Hyytiälä (HTL 11 spr)	PSM A09, DMPS, NAIS	17.3–16.5.2011	0.9–3.0
Hyytiälä (HTL 11 aut)	PSM A09, DMPS, NAIS	23.8–11.9.2011	1.1–3.0
Hyytiälä (HTL 12)	PSM A09, DMPS, NAIS	19.4–9.5.2012	1.3–3.0
Hyytiälä (HTL 13)	PSM A10, DMPS, NAIS	1.5–23.7.2013	1.3–3.0
Hyytiälä (HTL 14)	PSM A11, DMPS, NAIS	3.4–30.5.2014	1.0–3.0
Hyytiälä (HTL 15)	PSM A11, DMPS, NAIS	8.5.2015–30.4.2016	1.1–3.0
San Pietro Capofiume (SPC)	PSM A09, DMPS, NAIS	16.6–9.7.2012	1.5–3.0
Puy de Dôme (PDD)	PSM A09, SMPS, NAIS	16.1–29.2.2012	1.3–2.5
Brookhaven (BRH)	PSM A09*, SMPS	22.7–14.8.2011	1.3–3.0
Kent (KNT)	PSM A09*, SMPS	15.12.2011–6.1.2012	1.3–3.0
Centreville (CTR)	PSM A09, SMPS	1.6–15.7.2013	1.1–2.1
Shanghai (SH)	PSM A11	25.11.2013–23.1.2014	1.3–3.0
Nanjing (NJ)	PSM A11, NAIS	1.12.2014–31.1.2015	1.1–3.0
Helsinki (HEL)	PSM A11, DMPS	8.1.2015–31.12.2015	1.1–3.0

*The PSM was not operated in the scanning mode.

3.2 Data analysis

3.2.1 Particle formation rates

The primary quantities used for characterizing atmospheric new particle formation events are particle formation rate (J) and growth rate (GR) (Kulmala et al., 2012). The particle formation rate describes the rate at which new particles are formed in the atmosphere (in units $\text{cm}^{-3} \text{s}^{-1}$) and the particle growth rate describes how fast particles grow to larger sizes (in units nm/h). Both quantities can be estimated from measured or simulated particle size distribution data.

The particle formation rate is mathematically defined, for any size, as the flux of particles growing past that size (Kulmala et al., 2004a). The time evolution of particle concentration N_i in size bin i can be written as

$$\frac{dN_i}{dt} = J_{i-1,i} - J_{i,i+1} - S_i. \quad (1)$$

Here $J_{i-1,i}$ is the flux coming to size bin i from the previous bin $i-1$, representing the particle formation rate in size bin i . $J_{i,i+1}$ is the flux from bin i to bin $i+1$, and S_i describes the external sink for size bin i . In the atmosphere the external sink is mainly due to the coagulation of particles in size bin i with larger aerosol particles, which is commonly described by coagulation sink ($CoagS_i$) calculated from particle size distribution data (Kulmala et al., 2001). Thus, the sink term can be expressed as $S_i = CoagS_i \cdot N_i$.

Equation 1 can be obtained by integrating the continuous general dynamic equation (GDE; Friedlander, 1977) for aerosols, including only the growth and sink terms. When taking a traditional continuous approach and assuming that particles grow synchronously by condensation, one can write

$$J_{i,i+1} = n \cdot GR \Big|_{\text{at the boundary between bins } i \text{ and } (i+1)} \quad (2)$$

where n is the number concentration distribution function dN/dD_p and GR is the growth rate dD_p/dt .

If presuming that the assumptions behind Eq. (2) are valid, and approximating n at the lower bin boundary, Eq. (2) becomes

$$J_{i,i+1} = \frac{GR_{i,i+1}}{\Delta D_{p,i}} \cdot N_i \quad (3)$$

Thus, by combining Eqs. (1) and (3) and rearranging the terms, the following expression for the particle formation rate in size bin i is obtained:

$$J_{i-1,i} = \frac{dN_i}{dt} + \frac{GR_{i,i+1}}{\Delta D_{p,i}} \cdot N_i + CoagS_i \cdot N_i \quad (4)$$

By applying Eq. (4), the particle formation rate in a certain size bin can be calculated, if the time evolution of the concentration in the bin, the growth rate of particles out of the bin, and

the coagulation sink are known. In this thesis, Eq. (4) was utilized for calculating particle formation rates from measured particle size distribution data in **Papers II** and **IV**.

When calculating the formation rates of electrically charged particles, one needs to consider two additional processes affecting their concentration: the loss of ions due to ion–ion recombination and the production of ions due to charging of neutral particles. Taking these processes into account, the formation rate of positive (+) and negative (–) ions in size bin i can be expressed as:

$$J_{i-1,i}^{\pm} = \frac{dN_i^{\pm}}{dt} + \frac{GR_{i,i+1}}{\Delta D_{p,i}} \cdot N_i^{\pm} + CoagS_i \cdot N_i^{\pm} + \alpha \cdot N_i^{\pm} \cdot N_{<i}^{\mp} - \beta \cdot N_i \cdot N_{<i}^{\pm}. \quad (5)$$

Here α is the ion–ion recombination coefficient and β the ion-neutral attachment coefficient, for which the values of $1.6 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ and $0.01 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ are commonly used (Hoppel and Frick, 1986; Tammet and Kulmala, 2005). In reality, these coefficients are not constant but their values may depend on the chemical composition of ions or environmental conditions (Bates, 1985; Hoppel and Frick, 1986). Recently, Franchin et al. (2015) studied the ion–ion recombination coefficient experimentally in the CLOUD chamber, and found that the recombination coefficient increased with decreasing temperature and relative humidity (RH). Their experimentally determined recombination coefficient was closest to the value of $1.6 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ at temperature of 5 °C and RH of 40%. In this thesis, Eq. (5) was used for calculating the formation rates of ions in **Papers II** and **IV**.

3.2.2 Particle growth rates

As shown in the previous section, the particle growth rate can be used for describing particle flux in formation rate calculations. In addition, the growth rate can be used to derive the particle formation rate below the detection limit of the used aerosol instrument if the particle formation rate at a larger size and the losses due to coagulation are known (Kerminen and Kulmala, 2002; Lehtinen et al., 2007). The growth rate is also a key quantity when determining how large fraction of freshly-formed particles is able to survive to climatically relevant sizes before being lost due to coagulation (Pierce and Adams, 2007; Kuang et al., 2009). Furthermore, the growth rate can be used to estimate the concentration of condensing vapor (Nieminen et al., 2010). Correspondingly, if the condensing vapor concentration is known, it can be used to derive the growth rate.

As the particle growth rate has several different uses, it can also be determined from measured or simulated data using different methods. In **Papers II, IV and V** the particle growth rates were determined from experimental data, while in **Paper VI** three different methods to determine the growth rate were compared by using simulated particle size distribution data.

If the particle flux past a certain size is known, for example from model simulations, one can determine the growth rate corresponding to the flux (flux-equivalent growth rate, FGR) by rearranging Eq. (3) (Olenius et al., 2014):

$$\text{FGR}_{i,i+1} = \frac{J_{i,i+1}}{N_i} \Delta D_{p,i} \quad (6)$$

In this thesis, FGR was determined from Eq. (6) in **Paper VI** using the simulated particle size distribution data and it was then compared with the two other growth rate definitions discussed below. Earlier, Olenius et al. (2014) compared FGR to the growth rate determined from appearance times of particles (see below) and concluded that these two growth rates can significantly differ from each other, depending on the ambient conditions. However, they investigated only an ideal case, where the growth proceeds by monomer attachments and cluster-cluster collisions are not considered.

The growth rate can also be determined by considering the mass flux due to irreversible condensation of vapor onto an individual particle. This condensational growth rate (CGR) in size bin i can be calculated from (Nieminen et al., 2010):

$$\text{CGR}_{i,i+1} = \frac{\gamma}{2\rho} \left(1 + \frac{D_{\text{mon}}}{D_{p,i}}\right)^2 \left(\frac{8k_B T}{\pi}\right)^{1/2} \left(\frac{1}{m_{p,i}} + \frac{1}{m_{\text{mon}}}\right)^{1/2} m_{\text{mon}} C_{\text{mon}}. \quad (7)$$

Here C_{mon} is the vapor monomer concentration, ρ is the condensed phase density, $D_{p,i}$ and D_{mon} are the diameters of the particle and the vapor monomer and $m_{p,i}$ and m_{mon} are their masses. γ is a correction factor that is needed if CGR is calculated in the continuum regime. In this thesis, Eq. (7) was used to determine the growth rate due to the condensation of sulfuric acid in **Papers II** and **V** using the measured sulfuric acid concentration and in **Paper VI** using the simulated vapor monomer concentration.

The growth rate can also be determined by following the time evolution of particle size distribution in different ways. One method is based on determining the times at which particle concentration in each size bin reaches its maximum (Lehtinen and Kulmala, 2003; Hirsikko et al., 2005). The moments of maximum concentration can be determined by fitting a Gaussian distribution to the concentration time series at each size. Then, the growth rate can be retrieved as the slope of a linear least-square fit to the moments of maximum concentrations and the corresponding particle diameters. This method has been used to determine growth rates from ion size distribution data in several previous studies (e.g. Hirsikko et al., 2005; Manninen et al., 2009b; Yli-Juuti et al., 2011) and it was applied to NAIS data in **Papers II** and **IV**.

If the particle size distribution approaches a time-independent steady state, as is often the case in chamber experiments, the maximum concentration method cannot be applied. Alternatively, the growth rate can be determined based on the appearance times of particles (t_{app}). The appearance time growth rate (AGR) is obtained as the slope of a linear least-square fit to the appearance times of different-sized particles and the corresponding diameters. The fit can be applied to (t_{app}, D_p) data over several size bins, or then AGR can be determined for an individual size bin with the mean diameter $D_{p,i}$ from

$$\text{AGR}_{i,i+1} = \frac{D_{p,i+1} - D_{p,i}}{t_{\text{app},i+1} - t_{\text{app},i}}. \quad (8)$$

The appearance time of the size bin can be selected in different ways. One possibility is to define t_{app} as the time at which the concentration of the bin reaches 50% of the maximum

concentration in that size bin. This approach was used in **Papers II, V, and VI** when the growth rate was determined using the measured (**Paper II**) and simulated particle size distributions (**Paper V and VI**). Also, t_{app} can be defined as the time when the first particles are detected with a certain instrument cut-off size. In this case the diameters corresponding to t_{app} are the cut-off diameters of the instrument. This approach was utilized in **Paper V** for the growth rates determined from PSM data in chamber experiments. Lehtipalo et al. (2014) studied the robustness of the AGR method using aerosol dynamics model simulations and concluded that the method is generally rather insensitive to the choice of t_{app} .

3.2.3 Ion-ion recombination

To understand the role of ions in the dynamics of sub-3 nm particles, it is essential to know the contribution of recombination products to sub-3 nm particle concentrations. The size distribution of recombination products can be determined by utilizing measured ion size distributions.

The time evolution of the concentration of recombination products N_{rec} in size bin i can be expressed as

$$\begin{aligned} \frac{dN_{rec,i}}{dt} = & \lambda_i \alpha \sum_{j,k} r_{ijk} N_j^+ N_k^- - \beta N_{rec,i} (\sum_j N_j^+ + \sum_j N_j^-) - CoagS_i N_{rec,i} \\ & + \frac{N_{rec,i-1}}{\Delta D_p} GR_{i-1} - \frac{N_{rec,i}}{\Delta D_p} GR_i \end{aligned} \quad (9)$$

Here α is the ion-ion recombination coefficient and β the ion-neutral attachment coefficient, which were already discussed in the connection with Eq. (5). The coefficient λ_i is the fraction of stable recombination products that do not fragment instantly after their formation. N_j^+ and N_k^- are the concentrations of positive and negative ions in size bins j and k , and r_{ijk} tells the fraction of the recombination products that are formed in their collisions and end up in size bin i . $CoagS_i$ refers to the coagulation sink. GR_{i-1} and GR_i denote the growth rates of particles from size bins $i-1$ and i to the adjacent size bins due to condensation and ΔD_p is the width of the size bin (see also Eq. (3)). The terms in Eq. (9) describe different processes affecting the concentration of the recombination products in size bin i : their production in the collisions between oppositely charged ions (the first term on the right hand side), their loss due to charging (the second term), their loss due to coagulation (the third term) and their gain and loss due to condensational growth (the fourth and the fifth terms).

By assuming a pseudo steady state, the concentration of recombination products $N_{rec,i}$ can be solved from Eq. (9), which results in

$$N_{rec,i} = \frac{\lambda_i \alpha \sum_{j,k} r_{ijk} N_j^+ N_j^-}{CoagS_i + \beta (\sum_j N_j^+ + \sum_j N_j^-) + \frac{GR_i}{\Delta D_p} \left(1 - \frac{GR_{i-1}}{GR_i} \frac{N_{rec,i-1}}{N_{rec,i}} \right)} \quad (10)$$

When comparing the magnitudes of the terms in the denominator of Eq. (10), one can observe that with the typical values of air ion concentrations (Hirsikko et al., 2011) and the

coagulation sink in the lower troposphere, $CoagS_i \gg \beta(\sum_j N_j^+ + \sum_j N_j^-)$. Therefore, a simplified expression for the recombination product concentration can be obtained:

$$N_{rec,i} = \frac{\lambda_i \alpha \sum_{j,k} r_{ijk} N_j^+ N_k^-}{CoagS_i + \frac{GR_i}{\Delta D_p} \left(1 - \frac{GR_{i-1}}{GR_i} \frac{N_{rec,i-1}}{N_{rec,i}} \right)} \quad (11)$$

When looking at Eq. (11), one can notice that if the flux to the smallest size bin due to condensational growth is assumed to be negligible, it is possible to analytically solve $N_{rec,i}$ from Eq. (11). However, the growth rates of sub-3 nm particles in different size bins are not always available, at least with the required accuracy. For this reason, in **Papers II** and **IV** and in previous studies (Kulmala et al., 2007; Lehtipalo et al., 2009, 2010), the effect of condensational growth on the recombination product concentration is assumed to be negligible compared to the effect of coagulation sink. With this assumption, the recombination product concentration can be simply calculated from

$$N_{rec,i} = \frac{\lambda_i \alpha \sum_{j,k} r_{ijk} N_j^+ N_k^-}{CoagS_i} \quad (12)$$

In **Paper III** the size distribution of recombination products was, for the first time, calculated from Eq. (11) by considering the effect of condensational growth. The growth rates in the different size bins were obtained by fitting from the growth rates determined in **Paper II**. When utilizing Eqs. (11) and (12) to calculate the size distribution of recombination products, the recombination production rate (described by the term in the numerator) can be calculated from the ion size distribution data measured with the NAIS.

3.3 Cluster population simulations

To study the effect of cluster–cluster collisions on the growth of cluster population (**Papers V** and **VI**), and to compare different methods to determine particle growth rate (**Paper VI**), cluster population simulations were performed. The time evolution of the cluster population up to 70 clusters (corresponds to ~2 nm in mass diameter) was simulated in a one-component system with the Atmospheric Cluster Dynamics Code (ACDC; McGrath et al., 2012; Olenius et al., 2014). The model substance was assumed to have the properties of sulfuric acid-dimethylamine dimer in **Paper V** and the properties of sulfuric acid in **Paper VI**. The saturation vapor pressure of the model substance was set lower than the saturation vapor pressure of sulfuric acid to qualitatively mimic the stabilization of sulfuric acid clusters by base compounds.

The time evolutions of cluster concentrations were obtained by numerically solving their time derivatives, called birth-death equations (McGrath et al., 2012). The birth-death equations include all possible processes where a cluster can be formed or lost: the production of vapor monomers, the collisions and evaporations involving a cluster and a monomer, two monomers, or two clusters, and the loss of monomers and clusters due to an external sink. The collisions were considered as hard-sphere collisions and the collision rates were calculated from kinetic gas theory (Chapman and Cowling, 1952). The evaporation rates were

obtained from the Gibbs free energies of formation of the clusters, which were calculated from the classical one-component liquid droplet model (e.g. Ortega et al., 2012). In **Paper V** and in most of the simulations in **Paper VI**, the Gibbs free energy profile with a single maximum and no minima was assumed, in which case the stability of the clusters increases with the increasing size. In addition, in one simulation set in **Paper VI**, a free energy profile with a local minimum was used to study the system with elevated concentrations of stabilized small clusters. In most of the simulations in **Paper V**, where the aim was to simulate particle formation in the CLOUD chamber, the external sink was assumed to be due to the sticking of vapor monomers and clusters to the chamber walls according to Almeida et al. (2013). In **Paper VI** the external losses were assumed to have a power-law dependency on the cluster size, corresponding to the size-dependency of coagulation sink in the atmosphere (Lehtinen et al., 2007).

Several simulation sets were performed to study the effects of the vapor properties and environmental conditions on the growth of cluster population. The effect of cluster stability was studied by varying the saturation vapor pressure of the model substance (to which the evaporation rates are directly proportional), the effect of vapor concentration by varying the vapor source rate, and the effect of external sink by varying the magnitude of the sink. In **Paper V** the growth rates were determined from the time evolution of the simulated cluster distribution based on the appearance times of individual clusters (see Section 3.2.2). In **Paper VI** after simulating the time evolution of the cluster concentrations, the clusters were grouped into size bins containing an equal number of clusters (in most simulations ten) and the growth rates were determined for these size bins.

4 Atmospheric concentrations of sub-3 nm particles

The continuous presence of sub-2 nm ions in the atmosphere, formed as a result of ionization of air molecules, has been known already for decades (Hirsikko et al., 2011 and references therein). Kulmala et al. (2000) predicted theoretically that electrically neutral clusters also exist but due to the lack of technique to detect neutral sub-3 nm particles, this could not be verified for several years. However, thanks to the recent advancements in instrumental development, the number of observations of atmospheric sub-3 nm particles, including also neutral particles, has lately been increasing. This section includes first an overview of atmospheric observations of sub-3 nm particles, after which the results of this thesis on sub-3 nm particle concentrations are discussed.

The first atmospheric observations of sub-3 nm neutral particles were presented by Kulmala et al. (2007) based on the measurements at the SMEAR II station in Hyytiälä. By utilizing a NAIS and a prototype CPC, detecting particles down to 1.8 nm in mobility diameter, they proposed that a pool of neutral particles exist in the atmosphere, also outside particle formation events. Supporting their conclusion, Sipilä et al. (2008) also detected sub-2 nm neutral particles in Hyytiälä with a Pulse-Height CPC (PH-CPC) and an expansion CPC. Subsequently, Lehtipalo et al. (2009) deployed the PH-CPC in a field campaign in Hyytiälä over several months during spring 2007 and 2008. They observed a high number of sub-3 nm particles: their concentration varied between 500 and 50 000 cm⁻³ and reached the highest values at night. By comparing PH-CPC measurements to ion concentrations measured with a BSMA, they concluded that ions or their recombination products can explain only a minor fraction of sub-3 nm particles in Hyytiälä. Later, Lehtipalo et al. (2010) performed PH-CPC measurements in Mace Head, a coastal site in Ireland, and reported clearly lower sub-3 nm particle concentrations than in Hyytiälä. Utilizing ion size distribution measurements, they concluded that in Mace Head the contribution of ions and their recombination products to sub-3 nm particle concentrations is clearly higher than in Hyytiälä. However, it should be noted that all early methods used to detect sub-3 nm particles had several limitations. For example, the PH-CPC cannot measure sub-3 nm particle concentrations reliably when the concentrations are high (larger than 4000–5000 cm⁻³), and therefore this instrument may be inaccurate during new particle formation events or pollution episodes (Sipilä et al., 2009; Lehtipalo et al., 2010). In addition, the lowest particle size detected with the PH-CPC, or other CPCs used to measure sub-3 nm particles, could not be determined reliably until recently, due to the lack of proper calibration methods.

The development of DEG-based CPCs in recent years has enabled the measurements of atmospheric sub-3 nm particles down to ~1 nm in mobility diameter (Jiang et al., 2011; Vanhanen et al., 2011; Kuang et al., 2012a; Wimmer et al., 2013). Jiang et al. (2011) utilized a Scanning Mobility Particle Sizer (SMPS) equipped with a DEG-CPC to measure the size distribution of 1–10 nm particles during new particle formation in Atlanta, Georgia. They observed that DEG-SMPS data agreed well with the measurements of neutral clusters with a Cluster CIMS mass spectrometer. Subsequently, Zhao et al. (2011) deployed these two

instruments in a field campaign in Boulder, Colorado, and observed that during a new particle formation event the concentration of sub-2 nm particles measured with the DEG-SMPS increased simultaneously with the signals of clusters detected with the Cluster CIMS.

In this thesis, the concentrations of sub-3 nm atmospheric particles were measured with a PSM. Since the publication of **Paper II**, presenting the first atmospheric measurements with the PSM lasting for several months, there has been a growing number of studies reporting the results from PSM measurements from different environments. Yu et al. (2014) performed PSM measurements at two sites in the United States: at a continental site in Kent, Ohio, and at a coastal site in Brookhaven, New York. They observed at both sites elevated concentrations of sub-3 nm particles during daytime, associated with high sulfuric acid concentrations. In addition, in Brookhaven sub-3 nm particle concentrations increased also during some nights under the influence of marine air masses. Rose et al. (2015a) deployed a PSM and a NAIS at a mountain site in Puy de Dôme, France. Their results show that the concentrations of 1–2.5 nm neutral particles clearly exceeded those of charged particles during new particle formation both in the free troposphere and at the interface between the boundary layer and the free troposphere. In agreement with this, Bianchi et al. (2016) recently concluded based on PSM and NAIS measurements at a high-altitude site in Jungfraujoch, Switzerland, that neutral pathways dominate the formation of sub-3 nm particles in the free troposphere. Xiao et al. (2015) detected a high number of sub-3 nm particles at a strongly polluted urban site in Shanghai, China. They observed that sub-3 nm particle concentrations reached the highest values during daytime on new particle formation event days. Similar results were also obtained by Yu et al. (2016) from their PSM measurements in Nanjing, China.

4.1 Sub-3 nm particle concentrations in different environments

The size-segregated measurements of particle concentrations in the sub-2 nm size range were conducted by deploying a PSM in Hyytiälä during spring 2011 (**Paper II**). These measurements show that a high number of sub-2 nm particles is constantly present in Hyytiälä, which supports the earlier observations conducted with other instruments (Kulmala et al., 2007; Sipilä et al., 2008; Lehtipalo et al., 2009). The particle concentration between 0.9 and 2.1 nm size range typically varied between 1000 and 20 000 cm⁻³. The concentration was highest during daytime on new particle formation event days. Relatively high concentrations were still observed also at other times indicating that sub-2 nm particles are continuously formed in boreal forest.

After the findings in Hyytiälä, the PSM was deployed in San Pietro Capofiume during summer 2012 to investigate sub-3 nm particle concentrations in an environment with higher concentrations of anthropogenic pollutants than at a pristine boreal forest site (**Paper IV**). The measurements show that also in San Pietro Capofiume there exist a continuous population of sub-3 nm particles with the highest concentrations observed during new particle formation events. The particle concentrations were about 5 times higher in San Pietro Capofiume than in the same size range in Hyytiälä.

To obtain a more comprehensive picture of the concentrations of sub-3 nm particles in different environments, PSM data acquired at nine sites around the world were compared in **Paper I**. Some of these data were already published elsewhere but previously unpublished data were also included. The published data include measurements from Hyytiälä during spring 2011 (**Paper II**) and from San Pietro Capofiume (**Paper IV**), and measurements from Puy de Dôme (Rose et al., 2015a), Shanghai (Xiao et al., 2015), and Kent and Brookhaven (Yu et al., 2014). The unpublished data include measurements conducted in Hyytiälä during 2010–2016 and data from Helsinki, Centreville, and Nanjing. The overview of the measurements is presented in Table 1. To make the data sets as comparable as possible, the particle concentration between about 1 and 3 nm (referred to as sub-3 nm particle concentration) was determined for all the sites. It should still be noted that the measured size ranges were not identical in different measurements. In addition, measurements at different sites were conducted at different times of the year, and therefore the possible seasonality in sub-3 nm particle concentrations may bias the comparison.

The concentration of sub-3 nm particles was observed to vary between different environments (Table 2). The highest concentrations were detected at the sites with strong anthropogenic influence: in Chinese megacities Nanjing and Shanghai and in San Pietro Capofiume. In Finland sub-3 nm particle concentration was observed to be higher at the urban site located in Helsinki than at the boreal forest site in Hyytiälä. The lowest concentrations were detected at the high-altitude site in Puy de Dôme, France, and at three sites in the United States: Kent, Brookhaven, and Centreville. Thus, these results suggest that the formation of sub-3 nm particles is generally favored in polluted environments. This can be attributed to low-volatile precursor vapors which originate from anthropogenic sources, such as fuel combustion and traffic, and form small particles in the atmosphere (e.g. Arnold et al., 2012; Karjalainen et al. 2015; Sarnela et al., 2015). Some of the traffic-related particles may also be primary and produced inside car engines (Jayaratne et al., 2010; Alanen et al., 2015). The low sub-3 nm particle concentrations observed at the sites with little anthropogenic influence, such as in Puy de Dôme, can be explained by low concentrations of precursor vapors due to the absence of anthropogenic pollutant sources. On the other hand, in pristine environments the emissions of organic compounds from vegetation followed by their oxidation in the atmosphere may be an important source of low-volatile precursor vapors (Ehn et al., 2014). Finally, it should be noted that sub-3 nm particle concentrations detected in Brookhaven and Kent seem unexpectedly low compared with the observations at other urban measurement sites. This indicates that during these measurements the particle activation efficiency of the PSM may have been lower than in other measurement campaigns, which could have been caused by the chemical composition of particles or instrumental issues.

Table 2. Medians of sub-3 nm particle concentration, the ratio of the ion concentration to the total sub-3 nm particle concentration, sulfuric acid concentration, condensation sink, and the frequency of new particle formation (NPF) event days at different measurement sites. Sulfuric acid concentration was estimated from a proxy for all other sites except those that are marked with an asterisk (*). See Table 1 for the explanations of the abbreviations, the measurement periods and the exact size ranges for particle measurements. Data from Hyytiälä (HTL) and Helsinki (HEL) are divided into different seasons: spring (spr; March–May), summer (sum; June–August), autumn (aut; September–November), and winter (wint; December–February).

Measurement site	Sub-3 nm particle conc. (cm^{-3})	Ions to all sub-3 nm particles ratio	Sulfuric acid proxy (cm^{-3})	Condensation sink (s^{-1})	NPF event frequency (%)
HTL spr	2.9×10^3	0.16	1.0×10^6	2.6×10^{-3}	40
HTL sum	2.0×10^3	0.33	2.4×10^5	3.6×10^{-3}	19
HTL aut	7.9×10^2	0.83	2.6×10^5	2.0×10^{-3}	15
HTL wint	5.8×10^2	0.71	6.9×10^5	2.1×10^{-3}	0
SPC	8.5×10^3	0.004	1.0×10^7	1.2×10^{-2}	86
PDD	5.0×10^2	0.60	3.8×10^6	3.6×10^{-3}	23
BRH	8.0×10^2	-	$3.3 \times 10^5^*$	6.7×10^{-3}	17
KNT	4.7×10^2	-	$9.4 \times 10^5^*$	6.7×10^{-3}	22
CTR	5.9×10^2	0.47	$4.0 \times 10^4^*$	1.5×10^{-2}	9
SH	8.5×10^3	-	3.1×10^7	7.6×10^{-2}	21
NJ	1.7×10^4	0.02	2.0×10^7	2.7×10^{-2}	20
HEL spr	7.8×10^3	-	2.0×10^6	4.1×10^{-3}	13
HEL sum	5.1×10^3	-	2.5×10^6	5.3×10^{-3}	4
HEL aut	4.1×10^3	-	9.2×10^5	4.3×10^{-3}	12
HEL wint	6.9×10^3	-	2.2×10^5	3.6×10^{-3}	8

*Sulfuric acid concentration was measured.

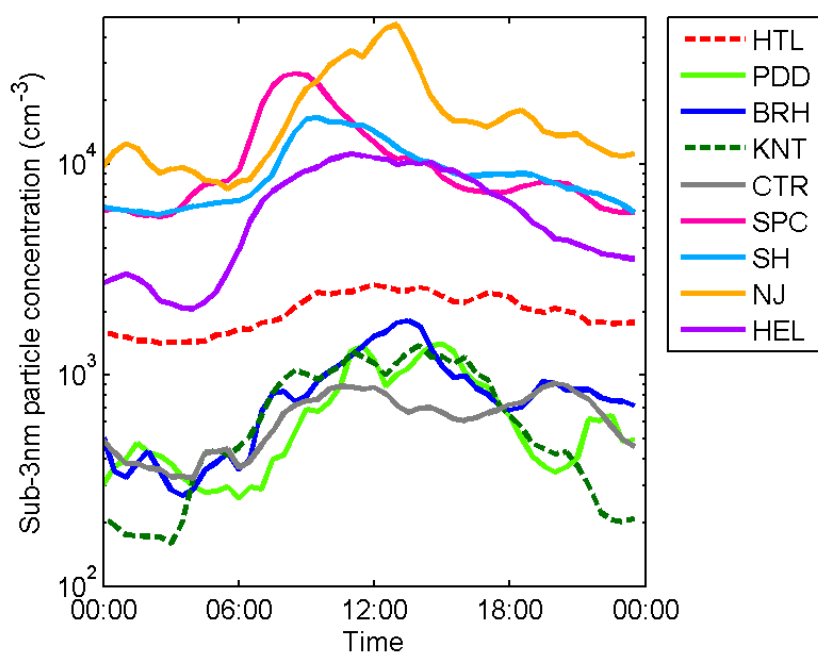


Figure 3. The median diurnal variation of sub-3 nm particle concentration at different sites: Hyytiälä (HTL), Puy de Dôme (PDD), Brookhaven (BRH), Kent (KNT), Centreville (CTR), San Pietro Capofiume (SPC), Shanghai (SH), Nanjing (NJ), and Helsinki (HEL). Figure adapted from **Paper I**.

Sub-3 nm particle concentration was observed to be highest during daytime and lowest at night at all the measurement sites (Fig. 3). The daytime maxima in sub-3 nm particle concentration have also been observed in previous studies (**Papers II** and **IV**; Yu et al., 2014, 2016; Rose et al., 2015a; Xiao et al., 2015), and they are likely linked to photochemical production of low-volatile precursor vapors or their emissions from different sources during daytime. However, at many of the measurement sites, sub-3 nm particle concentration was also relatively high in the evening or at night. This indicates that sub-3 nm particles can be formed in the absence of solar radiation, as a result of, for example, the oxidation of organic compounds by ozone or nitrate radical (Ehn et al., 2014). In previous field studies conducted in boreal forest, the concentrations of sub-3 nm particles and ions have been observed to often increase in the evening (Junninen et al., 2008; Lehtipalo et al., 2009, 2011; Buenrostro Mazon et al., 2016), which has been connected to the ozonolysis of monoterpenes (Lehtipalo et al., 2011). The recent results from the CLOUD experiment also suggest that monoterpenes ozonolysis products can form new particles without sulfuric acid (Kirkby et al., 2016). On the other hand, in Centreville, where the evening maximum was most obvious, the emissions of biogenic organic vapors from vegetation are dominated by isoprene (Xu et al., 2015). Furthermore, Yu et al. (2014) concluded that in Brookhaven the night-time maxima in sub-3 nm particle concentrations occurred only under the influence of marine air masses and they were likely not linked to the oxidation of monoterpenes.

At Finnish sites in Hyytiälä and Helsinki, measurements enabled to study the concentration of sub-3 nm particles in different size bins and during different seasons (Fig. 4). In Hyytiälä,

a clear seasonal cycle in sub-3 nm particle concentration could be observed with the highest concentration in summer and spring and the lowest in winter and autumn (see also Table 2). In the smallest size bin (1.1–1.3 nm), the concentration was clearly highest during summer. This may result from the high concentrations of low-volatile organic compounds at that time of the year, due to the emissions of organic vapors from vegetation and strong photochemical activity. In the largest size bin (2–3 nm), the highest concentrations were reached in spring. This indicates that in spring the conditions in Hyytiälä are favorable for the growth of particles, which is consistent with the high frequency of new particle formation events observed at that time of the year (Dal Maso et al., 2005; Nieminen et al., 2014). In Helsinki, the seasonal differences in sub-3 nm particle concentrations were subtler than in Hyytiälä and the concentrations were high also in winter in all four size bins. This implies that in Helsinki the formation of sub-3 nm particles is more likely driven by the vapors originating from anthropogenic pollutant sources than from biogenic sources, contrary to Hyytiälä. Furthermore, in Helsinki the increase in particle concentrations in the morning occurred at the same time in all seasons, which indicates that it is likely not linked to photochemistry but could be triggered by the morning traffic on the roads near the station (see Järvi et al., 2008).

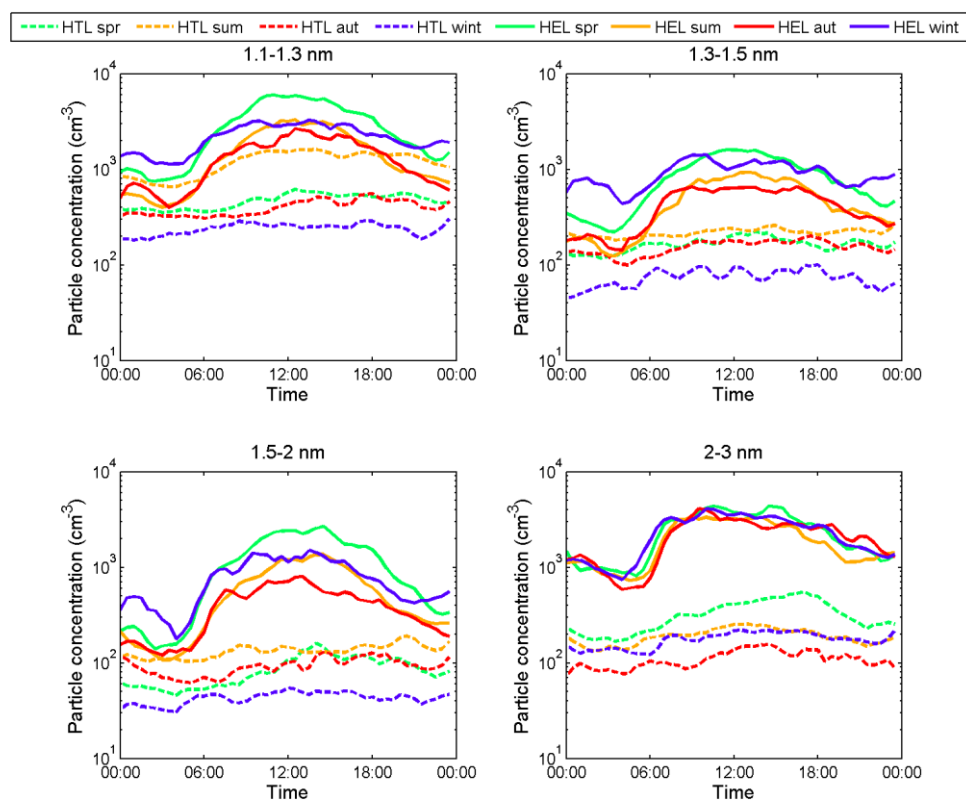


Figure 4. The median diurnal variation of particle concentration in four size bins (1.1–1.3 nm, 1.3–1.5 nm, 1.5–2 nm, and 2–3 nm) in Hyytiälä (HTL; dashed lines) in 2011 and 2015–2016 and in Helsinki (HEL; solid lines) in 2015. The data are divided into different seasons: spring (spr; March–May), summer (sum; June–August), autumn (aut; September–November), and winter (wint; December–February). Figure adapted from **Paper I**.

4.2 Contribution of ions to sub-3 nm particle concentrations

4.2.1 Fraction of ions of all sub-3 nm particles

To study the contribution of ions to the sub-3 nm particle population, ion concentrations measured with the NAIS were compared to the total sub-3 nm particle concentrations measured with the PSM. This was done for the first time using measurements conducted in Hyytiälä during spring 2011 (**Paper II**). The results from these measurements show that neutral pathways dominate the dynamics of sub-3 nm particles in Hyytiälä during spring. The contribution of ions to sub-3 nm particle concentrations was found to be minor especially during new particle formation events. Subsequently, similar results were obtained in the measurements in San Pietro Capofiume (**Paper IV**), where the concentrations of neutral sub-3 nm particles were found to exceed ion concentrations even more clearly than in Hyytiälä.

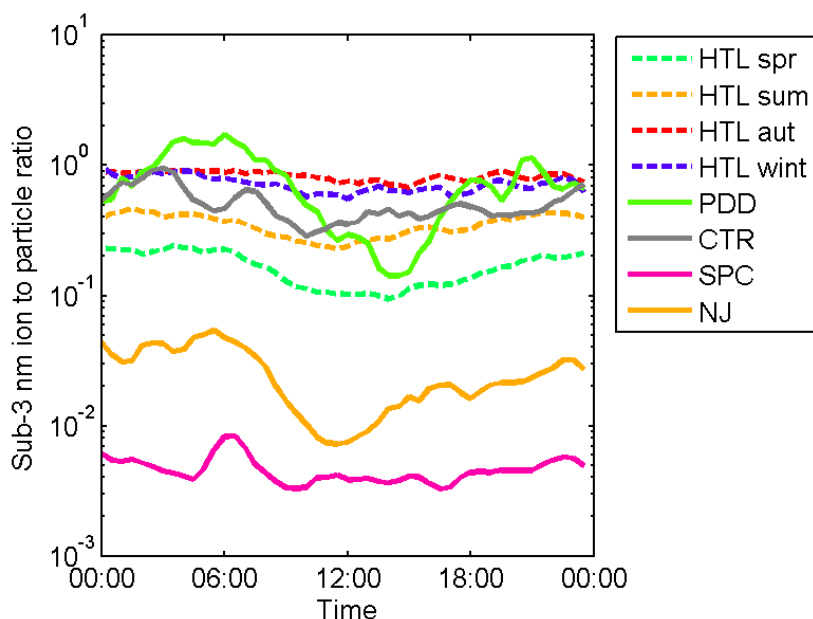


Figure 5. The median diurnal variation of the ratio of ion concentration to the total sub-3 nm particle concentration at different measurement sites: Hyytiälä (HTL), Puy de Dôme (PDD), Centreville (CTR), San Pietro Capofiume (SPC), and Nanjing (NJ). The data from Hyytiälä are divided into different seasons: spring (spr; March–May), summer (sum; June–August), autumn (aut; September–November), and winter (wint; December–February). Figure adapted from **Paper I**.

To investigate how the contribution of ions varies in different environments, the ratios of ion concentration to the total sub-3 nm particle concentration at several different measurement sites were compared in **Paper I**. The ion ratio was observed to be low at the sites with the high total sub-3 nm particle concentration (Table 2), which results from the smaller variation in ion concentration between different sites than in the total sub-3 nm particle concentration. The lowest ion ratios were detected in San Pietro Capofiume and Nanjing (the median values 0.004 and 0.02), while in Centreville and Puy de Dôme the ion ratios were relatively high (the median values 0.47 and 0.60). In Hyytiälä the ion ratio had a clear seasonal cycle: the ion ratio was relatively low in spring and summer (the median values 0.16 and 0.33) and high in autumn and winter (the median values 0.83 and 0.71). In Hyytiälä during autumn and winter, and in Puy de Dôme and Centreville, the ion ratio even exceeded unity relatively often, which shows that the PSM was not able to detect all 1–3 nm particles. This could result from uncertainties in the detection efficiency of the PSM related to the chemical composition of particles or environmental conditions. For example, the detection efficiency of the PSM has been observed to be significantly lower for organic clusters than for those containing sulfate (Kangasluoma et al., 2016a; see also discussion in Section 3.1.1.1).

The median diurnal cycle of the ratio of ion concentration to the total sub-3 nm particle concentration at different measurement sites is depicted in Fig. 5. As expected, the diurnal cycle of the ion ratio was opposite to that of the total sub-3 nm particle concentration: the ion ratio was lowest during daytime and highest in the early morning. When studying the ion ratio in different sub-3 nm size bins in Hyytiälä, the ion ratio was observed to be highest in the size bins below 2 nm. This can be explained by the pool of small ions constantly present in the atmosphere as a result of ionization of air molecules (Manninen et al., 2009a; Hirsikko et al., 2011). Overall, it seems that neutral particles dominate the sub-3 nm particle population in polluted environments and in boreal forest during spring and summer. However, more knowledge of the properties of atmospheric sub-3 nm particles and their activation in the PSM in different environmental conditions would be needed to be able to determine the ion ratios more reliably.

4.2.2 Recombination products

To obtain the complete picture of the role of ions in the dynamics of sub-3 nm particles, one also needs to study the importance of recombination products, formed in the collisions between oppositely charged ions. In **Papers II** and **IV** the contribution of recombination products to sub-3 nm particle concentrations was estimated in Hyytiälä during spring 2011 and in San Pietro Capofiume during summer 2012 using NAIS data. The concentrations of recombination products were calculated from Eq. (12), where only the recombination production rate and coagulation losses are considered and the effect of condensational growth is neglected. The results of these papers indicate that recombination products account only for a minor fraction of all electrically neutral sub-3 nm particles at these sites, which is in agreement with the observations of previous studies (Kulmala et al., 2007; Lehtipalo et al., 2009;

Manninen et al., 2009b). In Hyytiälä the median fraction of recombination products of all neutral sub-3 nm particles was found to vary between 0.3% and 5% in different size bins between 0.9 and 2.1 nm, while in San Pietro Capofiume the median fraction was less than 1% in the two sub-3 nm size bins.

In reality, the effect of condensational growth should be taken into account when determining the size distribution of recombination products. In **Paper III** this was done for the first time: the concentrations of recombination products in different size bins between 0.9 and 2.1 nm were calculated from Eq. (11) by utilizing the same data set from Hyytiälä as used in **Paper II**. The recombination production rate was observed to be highest between 1.3 and 1.7 nm, which can be explained by the maximum in ion concentration between 1.1 and 1.3 nm (Table 3). The concentration of recombination products was highest between 1.5 and 1.9 nm. When comparing the concentration of recombination products to the total concentration of electrically neutral particles, recombination products were observed to account, on average, for 1.5% of all neutral 0.9–2.1 nm particles. The fraction of recombination products of all neutral particles was lowest in the smallest size bin (the median value 0.2%) and highest between 1.5 and 1.9 nm (the median value 13%). Thus, also when taking into account the effect of condensational growth, recombination products can be concluded to have only a minor contribution to the total concentration of neutral sub-3 nm particles in boreal forest, at least during spring. In other seasons, especially in winter and autumn when the total sub-3 nm particle concentration in Hyytiälä is lower (see Section 4.1), the contribution of recombination products may be higher. The results also indicate that the effect of condensational growth on the size distribution of recombination products should not be neglected, if the values for the particle growth rate are known.

Table 3. The median values for the recombination production rate (R_r), the concentrations of recombination products (N_{rec}), all particles (N_{tot}), ions (N_{ions}), and all neutral particles ($N_{n,tot}$), and the fraction of recombination products of all neutral particles in six size bins in Hyytiälä during spring 2011.

size range (nm)	R_r ($\text{cm}^{-3} \text{ s}^{-1}$)	N_{rec} (cm^{-3})	N_{tot} (cm^{-3})	N_{ions} (cm^{-3})	$N_{n,tot}$ (cm^{-3})	$N_{rec}/N_{n,tot}$ (%)
0.9–1.1	9.0×10^{-3}	6	2955	174	2793	0.2
1.1–1.3	3.0×10^{-2}	24	1122	271	847	2.7
1.3–1.5	7.0×10^{-2}	56	873	183	653	8.0
1.5–1.7	6.0×10^{-2}	69	532	56	450	12.9
1.7–1.9	3.0×10^{-2}	69	470	16	447	13.0
1.9–2.1	7.0×10^{-3}	48	699	5	694	5.0

4.3 Effect of environmental conditions and connections to particle formation events

To understand how environmental conditions affect sub-3 nm particle concentrations, sulfuric acid concentration and condensation sink at different measurement sites were compared in **Paper I** (Table 2). Sulfuric acid concentration was estimated for most sites from a proxy (Petäjä et al., 2009; Mikkonen et al., 2011), and condensation sink, describing the loss rate of sulfuric acid due to condensing on aerosol particles, was calculated from particle size distribution data. The median sulfuric acid concentration was observed to be highest at the sites with the highest sub-3 nm particle concentrations, i.e. in Nanjing, Shanghai and San Pietro Capofiume. This indicates that the formation of sub-3 nm particles is favored in the presence of high sulfuric acid concentration, which is consistent with the numerous observations of the importance of sulfuric acid for atmospheric particle formation (e.g. Weber et al., 1995; Sihto et al., 2006; Kuang et al., 2008). On the other hand, in Nanjing, Shanghai, and San Pietro Capofiume, the median condensation sink was also high ($>10^{-2} \text{ s}^{-1}$), indicating high coagulation losses of small particles. Therefore, it seems that the concentration of sub-3 nm particles is determined by the availability of precursor vapors, such as sulfuric acid, rather than the value of the sink caused by pre-existing larger particles.

New particle formation events are characterized by the appearance of new particles with diameters of 3–25 nm and their further growth to larger sizes (Dal Maso et al., 2005). To investigate how the occurrence of these events is connected to the concentration of sub-3 nm particles, the event frequency at different measurement sites was studied (Table 2). Particle formation events were most frequent during the measurement campaign in San Pietro Capofiume (86% of the days were event days) and in Hyytiälä during spring (40% of the days were event days). In Hyytiälä the event frequency was lower in other seasons (0%–19%). In Helsinki the event frequency was highest in spring (13%) and lowest in summer (4%). In Puy de Dôme, Brookhaven, Kent, Shanghai, and Nanjing, the event frequency varied between 17% and 23%. In Centreville events occurred only on 9% of the days. Overall, when comparing the event frequencies to the concentrations of sub-3 nm particles at different measurement sites, no clear relation can be seen. Thus, the occurrence of particle formation events does not seem to be only determined by the concentration of sub-3 nm particles. This indicates that the formation of the smallest particles and their growth to larger sizes are two separate processes, as proposed already by Kulmala et al. (2000), and the growth occurs only in favorable conditions. These results also demonstrate that to understand the first steps of atmospheric particle formation and growth, detailed analysis of the dynamics of sub-3 nm particles in different size ranges is required.

5 First steps of new particle formation and growth

The first evidence of atmospheric particle formation was reported already in the 19th century by John Aitken. Since then new particle formation has been observed to be a frequent phenomenon in various locations around the world (Kulmala et al., 2004a). During the last decades, numerous studies, including field and laboratory measurements and modeling, have been conducted to investigate particle formation mechanisms and the role of different vapors in particle formation and growth (Zhang et al., 2012; Kulmala et al., 2014). In this section, the development of our understanding of atmospheric particle formation is first reviewed, after which the results of this thesis contributing to this topic are discussed.

The association between sulfuric acid and atmospheric particle formation was observed already decades ago (Weber et al., 1995; Weber et al., 1996). After that the importance of sulfuric acid in atmospheric particle formation has been demonstrated in various studies, showing the correlation between particle formation rates and sulfuric acid concentration in different environments (e.g. Sihto et al., 2006; Kuang et al., 2008; Paasonen et al., 2010; Wang et al., 2011). However, sulfuric acid concentrations required for the onset of particle formation in the boundary layer have been observed to be clearly lower than the corresponding values in most laboratory experiments of binary (sulfuric acid–water) nucleation (Berndt et al., 2005; Benson et al., 2008), although not in all (Sipilä et al., 2010). This indicates that other compounds besides sulfuric acid and water vapor are needed to explain atmospheric particle formation events.

Ammonia has been considered for a possible candidate for participating in particle formation, as it is able to stabilize sulfuric acid–water clusters and thus enhance particle formation rates (Coffman and Hegg, 1995; Weber et al., 1996; Ball et al., 1999). Kurtén et al. (2008) showed, based on theoretical calculations, that amines are able to stabilize clusters even more effectively than ammonia, which has later been observed in other theoretical and experimental studies (Berndt et al., 2010; Erupe et al., 2011; Ortega et al., 2012). Subsequently, Petäjä et al. (2011) proposed that the required concentrations of stabilizing compounds are very low, and thus the impurities of base compounds may have affected the results of some of the earlier nucleation experiments, such as those of Sipilä et al. (2010). Finally, a series of experiments in the CLOUD chamber enabled to quantify the effect of atmospherically relevant concentrations of ammonia and amines on particle formation rates. First, Kirkby et al. (2011) showed that at atmospherically relevant ammonia concentrations particle formation rates are more than 100–1000-fold compared with the sulfuric acid–water system. With the APi-TOF measurements, they were able to follow the formation of negatively charged sulfuric acid–ammonia clusters by stepwise additions of ammonia. Later, Almeida et al. (2013) showed that in a sulfuric acid–water–dimethylamine system particle formation proceeds with the similar base-stabilization mechanism, and particle formation rates are enhanced more than 1000-fold compared with the ammonia containing system. By deploying a CI-APi-TOF, Kürten et al. (2014) were able to follow the formation of electrically neutral sulfuric acid–dimethylamine clusters in the CLOUD chamber and concluded

that their formation proceeds near to or at kinetic limit. Earlier, Zhao et al. (2011) had also detected neutral clusters, likely composed of sulfuric acid and amines, first in the laboratory, by mixing ambient air with sulfuric acid, and later in the atmosphere. Altogether, it seems likely that ammonia or amines participate in atmospheric particle formation. However, the results indicate that ternary nucleation involving sulfuric acid, water and ammonia cannot explain particle formation rates observed in the boundary layer (Kirkby et al., 2011), and ternary nucleation including amines can explain particle formation rates only close to amine sources (Almeida et al., 2013). Therefore, some other vapors also need to be involved in atmospheric particle formation.

Low-volatile organic compounds have long been thought to account for the growth of nanometer-sized particles to larger sizes (Kulmala et al., 1998; Kulmala et al., 2001; O'Dowd et al., 2002), as in most environments the condensation of sulfuric acid cannot explain the observed particle growth (Iida et al., 2008; Kuang et al., 2012b; Riipinen et al., 2011, 2012). It has also been suggested based on both laboratory and field measurements that organic compounds may participate in the nucleation process (Bonn et al., 2008; Metzger et al., 2010; Paasonen et al., 2010; Riccobono et al., 2012). In the boreal forest these compounds could be highly oxidized monoterpenes oxidation products (Ehn et al., 2012). Schobesberger et al. (2013) deployed an API-TOF in the CLOUD chamber and found that the oxidation products of monoterpenes can indeed form clusters with sulfuric acid molecules, which grow further by additions of both sulfuric acid and organic molecules. Furthermore, particle formation involving sulfuric acid and oxidized organic compounds produces similar particle formation rates as observed in the boundary layer (Riccobono et al., 2014). By utilizing a CI-API-TOF, Ehn et al. (2014) showed that low-volatile oxidation products of monoterpenes are formed at a significant mass yield and that they may participate in the first steps of particle formation as well as explain the growth of freshly-formed particles to climatically relevant sizes. Recently, it was observed in the CLOUD chamber that the oxidation products of monoterpenes can form clusters even without sulfuric acid (Kirkby et al., 2016). The pure biogenic particle formation could also occur in the atmosphere in the conditions with low sulfuric acid concentration.

The possible role of ions in atmospheric particle formation has been recognized for a long time due to their ability to stabilize small clusters and form neutral clusters by ion-ion recombination (e.g. Arnold et al., 1982; Yu and Turco, 2000; Kazil et al., 2008 and references therein). Field measurements, conducted by utilizing ion mobility spectrometers, suggest that the contribution of ion-mediated processes to particle formation is only minor, less than 10%, in the boundary layer (Iida et al., 2006; Manninen et al. 2010; Hirsikko et al., 2011), and slightly higher at mountain sites (Boulon et al., 2010; Manninen et al., 2010; Rose et al., 2015b). Still, it should be noted that in these studies particle formation has been studied at about 2 nm size, and thus, in principle, particles could have been formed by charged mechanisms before being neutralized. Based on model simulations and aircraft measurements, it has been suggested that ion-mediated mechanisms could be important in the upper parts of the troposphere and in the stratosphere, where temperature and aerosol surface area are low and ionization rate and sulfuric acid concentration high (Lee et al., 2003; Yu et al.,

2010; Arnold et al., 2008). However, recent studies deploying a PSM and a NAIS at high-altitude measurements sites indicate that neutral pathways dominate particle formation also in the free troposphere (Rose et al., 2015a; Bianchi et al., 2016). The CLOUD experiments have enabled the quantification of the effect of ions on particle formation rates in different conditions. The results indicate that in the systems containing sulfuric acid and stabilizing agents (ammonia, amines or oxidized organic compounds), the enhancement of particle formation rates due to ions is small, unless the overall particle formation rates are low (Kirkby et al., 2011; Almeida et al., 2013; Riccobono et al., 2014). However, when particle formation is driven by organic compounds in the absence of sulfuric acid, ions can enhance particle formation rates by one or two orders of magnitude (Kirkby et al., 2016).

In addition to the role of different atmospheric constituents, meteorological conditions favoring particle formation have been widely researched. Solar radiation has been observed to be important for atmospheric particle formation in numerous studies (e.g. Birmili and Wiedensohler, 2000; Boy and Kulmala, 2002; Nieminen et al., 2015), reflecting the significance of photochemical oxidation processes producing low-volatile vapors. In most environments particle formation events only occur during daytime (Kulmala et al., 2004a), although bursts of sub-3 nm neutral and charged particles may take place at night (Lehtipalo et al., 2011; Buenrostro Mazon et al., 2016). In some locations particle formation and growth events have also been detected at night (Suni et al., 2008; Svenningsson et al., 2008; Kalivits et al., 2012). The conditions with low relative humidity and low pre-existing aerosol surface area have been observed to favor particle formation in the boundary layer (Hyvönen et al., 2005; Hamed et al., 2011; Nieminen et al., 2015). Furthermore, it has been suggested that particle formation may be induced by the turbulent mixing of boundary layer (Nilsson et al., 2001; Wehner et al., 2010). In the free troposphere particle formation has been observed to be often triggered by dynamic processes, such as deep convection, mixing in the cloud outflow regions, and the exchange of air between troposphere and stratosphere (Clarke et al., 1998; Twohy et al., 2002; Young et al., 2007).

5.1 Particle formation

5.1.1 Particle formation rates

To investigate the first steps of atmospheric particle formation, particle formation rates were studied in **Papers II** and **IV** based on the measurements conducted in Hyytiälä during spring 2011 and in San Pietro Capofiume during summer 2012. The formation rates were calculated from Eqs. (4) and (5) using measured particle and ion size distribution data. The diurnal variation of formation rates for different-sized particles and ions is shown in Fig. 6 for new particle formation event and non-event days.

In Hyytiälä the formation rates of ions and particles showed only little diurnal variation on non-event days. The formation rates of 1.5-nm positive ions and negative ions were about $0.01 \text{ cm}^{-3} \text{ s}^{-1}$. The formation rates of 1.5-nm and 2-nm particles were slightly above $0.1 \text{ cm}^{-3} \text{ s}^{-1}$, while the formation rate of 3-nm particles was most of the time too low to be detected. On event days, the formation rates of 1.5-nm ions were slightly higher than on non-

event days, around $0.05 \text{ cm}^{-3} \text{ s}^{-1}$, staying rather constant throughout the day. However, the formation rates of 1.5-, 2- and 3-nm particles had pronounced maxima around noon on event days. At this time the formation rate of 1.5-nm particles approached the value of $\sim 4 \text{ cm}^{-3} \text{ s}^{-1}$, exceeding the formation rate of ions by a factor of 50–100. The formation rate of 3-nm particles approached the formation rate of 2-nm particles around noon and was over two orders of magnitude higher than at the same time on non-event days.

In San Pietro Capofiume particle formation rates were higher than in Hyytiälä but their behavior was quite similar. On non-event days the formation rate of 1.6-nm particles was slightly below $10 \text{ cm}^{-3} \text{ s}^{-1}$ throughout the day and the formation rate of 2-nm particles about $1 \text{ cm}^{-3} \text{ s}^{-1}$. The formation rates of 1.6-nm ions were about $0.1 \text{ cm}^{-3} \text{ s}^{-1}$ and the formation rates of 2-nm ions slightly lower than that. On event days, the particle formation rates had maxima in the morning around 9:00. At this time the formation rate of 1.6-nm and 2-nm particles approached the values of $70 \text{ cm}^{-3} \text{ s}^{-1}$ and $7 \text{ cm}^{-3} \text{ s}^{-1}$. The formation rates of ions were only slightly higher than on non-event days, and thus clearly lower than the total particle formation rates.

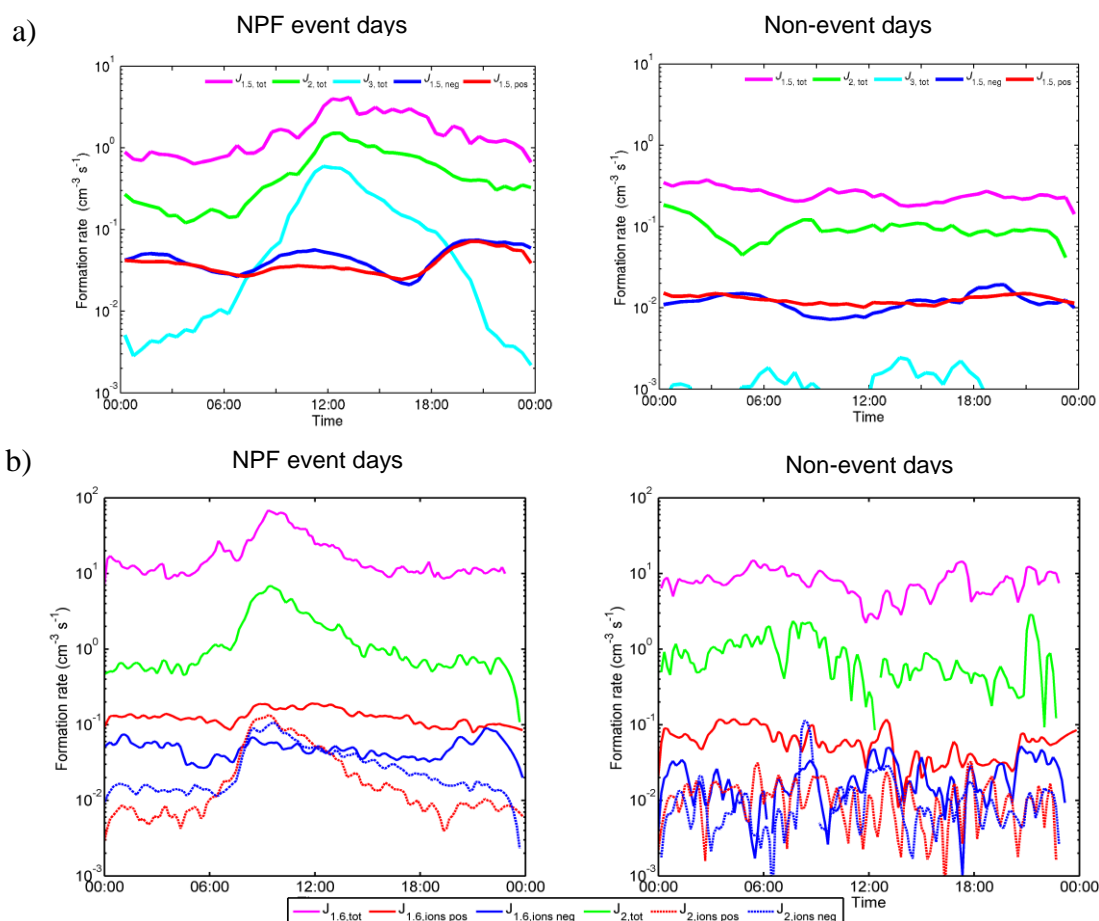


Figure 6. Median diurnal cycle of the formation rates of different-sized particles and ions on new particle formation (NPF) event and non-event days a) in Hyytiälä during spring 2011 and b) in San Pietro Capofiume during summer 2012. In the legends, the numbers in the subscripts refer to the size in nanometers, and “tot” refers to all particles, “pos” to positive ions and “neg” to negative ions. Figure adapted and modified from **Papers II** and **IV**.

As the total particle formation rates clearly exceeded the ion formation rates in Hyytiälä and San Pietro Capofiume, neutral pathways seem to dominate particle formation at both sites. This is in agreement with the earlier studies, where the contribution of ions to the total particle formation rate has been estimated to be less than 10% in boreal forest based on NAIS measurements (Kulmala et al., 2007; Manninen et al., 2009b). Furthermore, the higher values of formation rates observed in San Pietro Capofiume than in Hyytiälä indicate that the formation of neutral particles is favored in polluted environment with high concentrations of low-volatile precursor vapors. This is also supported by the results of Xiao et al. (2015) who detected high particle formation rates in Shanghai, China. Furthermore, in **Paper I** sub-3 nm particle concentrations were observed to be higher at the sites with strong anthropogenic influence than in cleaner environments (see Section 4.1).

The relatively high formation rates of 1.5–1.6 nm particles observed in Hyytiälä and San Pietro Capofiume outside particle formation events indicate that the smallest, sub-2 nm particles (or molecular clusters) can be formed in the atmosphere constantly. This is also consistent with the results of **Paper I** (see Section 4.1). On the other hand, the formation rate of 3-nm particles was observed to reach measurable values only during particle formation events. This implies that the main factor limiting the occurrence of particle formation events is the growth of particles from sub-2 nm sizes to 3 nm. The particle growth is discussed more in Section 5.2.

5.1.2 Role of different vapors in particle formation

The role of different vapors in atmospheric particle formation can be studied by investigating their correlation with particle formation rates or with the concentrations of newly-formed particles. In **Paper II**, correlations between sub-2 nm particle concentrations and gaseous compounds detected with chemical ionization mass spectrometers were investigated based on measurements conducted in Hyytiälä during spring 2011. A clear positive correlation between the concentrations of electrically neutral particles and sulfuric acid was observed: the correlation coefficient R was 0.6–0.8 in different sub-2 nm size bins. In addition, particle formation rates also correlated with sulfuric acid concentration. These correlations suggest that sulfuric acid participates in particle formation in boreal forest, as also concluded in several earlier studies (e.g. Sihto et al., 2006; Riipinen et al., 2007; Nieminen et al., 2009). Furthermore, sub-2 nm particle concentration was observed to correlate with highly oxidized organic compounds detected with the CI-APi-TOF. The positive correlation was clear especially with the nitrate containing organic compound $C_{10}H_{15}O_8N$ detected at the mass 339 Th ($R = 0.6$ – 0.7 in different sub-2 nm size bins). When studying only new particle formation event days, sub-2 nm particle concentration also correlated with the total concentration of highly oxidized organic molecules in the 300- to 450-Th mass range ($R = 0.5$ – 0.7 in different sub-2 nm size bins). This indicates that highly oxidized organic compounds may also be precursors for sub-2 nm particles in boreal environment, which is in agreement with the results of recent chamber experiments (Schobesberger et al., 2013; Ehn et al., 2014).

To obtain a broader picture of the effects of different gaseous compound on sub-3 nm particle concentrations, correlations between particle concentrations in the 1–3 nm size range and different variables were studied at several different measurement sites in **Paper I** (Table 4). In Hyytiälä and Helsinki correlations were studied separately in the 1.1–2 nm and 2–3 nm size ranges. Sub-3 nm particle concentration was observed to have a moderate positive correlation with sulfuric acid concentration (estimated for most sites from a proxy): at other sites than Hyytiälä the correlation coefficient R was between 0.31 and 0.44. Thus, although sulfuric acid is likely involved in the formation of sub-3 nm particles, their concentrations also seem to depend on other factors. On the other hand, the uncertainties in the proxy used for estimating sulfuric acid concentration may significantly deteriorate correlations. In Hyytiälä, the correlation depended strongly on the size range: the particle concentration in the 1.1–2 nm size range did not correlate with sulfuric acid concentration ($R = 0.02$), while the particle concentration in the size range of 2–3 nm correlated ($R = 0.38$). This could indicate that in Hyytiälä the formation of sub-2 nm particles is mainly driven by some other vapor than sulfuric acid. Still, sulfuric acid is likely needed for the growth of newly-formed particles to larger sizes, as several previous studies highlight the importance of sulfuric acid for particle formation in boreal forest (e.g. Sihto et al., 2006; Riipinen et al., 2007; Nieminen et al., 2009). Furthermore, as discussed above, when using data from spring 2011 and measured sulfuric acid concentration, a positive correlation between sub-2 nm particles and sulfuric acid concentration can be observed (**Paper II**). This could indicate that the role of sulfuric acid is more important during spring, or imply the uncertainties in the proxy.

The measurements of low-volatile organic vapors were not available for most of the measurements sites, and thus their correlation with particle concentrations could not be investigated. However, to indirectly estimate the importance of organic compounds, the correlation between sub-3 nm particles and temperature was studied, as temperature usually drives the emissions of organic compounds from vegetation (Günther et al., 2012). Interestingly, sub-3 nm particle concentration was observed to have a clear positive correlation with temperature at some of the measurement sites. The positive correlation was strongest in Hyytiälä, San Pietro Capofiume and Shanghai, possibly indicating that at these sites biogenic organic compounds are important for the formation of sub-3 nm particles. In Hyytiälä, the positive correlation could be observed only in the 1.1–2 nm size range ($R = 0.61$), whereas particles in the 2–3 nm size range did not correlate with temperature ($R = 0.05$). This implies that in Hyytiälä low-volatile organic vapors are essential especially for the formation of the smallest, sub-2 nm particles, which would also explain the summertime maximum in their concentration (see Section 4.1). On the other hand, one should not draw too broad conclusions on the role of organic compounds only based on correlations with temperature. For instance, the low correlation observed in the 2–3 nm size range in Hyytiälä does not mean that organic compounds cannot be important in this size range. In addition, it should be noted that the correlation between sub-3 nm particles and temperature may also, at least partly, reflect the correlation between sub-3 nm particles and solar radiation, as radiation and temperature usually correlate with each other.

In Hyytiälä and Helsinki, the correlation between sub-3 nm particle concentration and nitrogen oxides (NO and NO_x), which are tracers for traffic emissions, were also investigated. In Hyytiälä sub-3 nm particle concentration was observed to have a negative correlation with NO_x in the 1.1–2 nm size range ($R = -0.45$), while no relation between particle concentrations and NO was found. However, in Helsinki sub-3 nm particle concentration had a positive correlation with the concentrations of NO and NO_x. The correlation was stronger in the 1.1–2 nm size range ($R = 0.51$ for NO and $R = 0.39$ for NO_x) than in the 2–3 nm size range. This indicates that sub-3 nm particles observed in Helsinki may be linked to vehicle emissions on the roads near the station. This conclusion is also supported by the diurnal cycle of sub-3 nm particle concentration in Helsinki (see Section 4.1).

Table 4. Pearson’s correlation coefficients between sub-3 nm particle concentration and different variables: sulfuric acid concentration (estimated from a proxy for most sites), temperature, and NO and NO_x concentrations. In Hyytiälä (HTL) and Helsinki (HEL), the correlation is shown separately for two size ranges (1.1–2 nm and 2–3 nm).

Measurement site	Sulfuric acid conc.	Temperature	NO conc.	NO _x conc.
HTL 1–2 nm	0.02	0.61	−0.14	−0.45
HTL 2–3 nm	0.38	0.05	0.13	−0.05
HEL 1–2 nm	0.24	−0.09	0.51	0.39
HEL 2–3 nm	0.25	−0.02	0.34	0.31
SPC	0.43	0.56	-	-
PDD	0.37	0.12	-	-
SH	0.27	0.44	-	-
NJ	0.48	0.22	-	-
BRH	0.44*	0.29	-	-
KNT	0.39*	−0.01	-	-
CTR	0.31*	0.24	-	-

*Sulfuric acid concentration was measured.

5.2 Growth rates of sub-3 nm particles

5.2.1 Sub-3 nm particle growth rates observed in the atmosphere

The results of this thesis indicate that the formation of new particles in the atmosphere is mainly limited by the growth of particles in the 1–3 nm size range (see Section 5.1.1). To investigate the initial particle growth, the average growth rate of sub-3 nm particles was determined from data measured in Hyytiälä during spring 2011 (**Paper II**; Fig. 7). The growth rate was determined for different size ranges by applying the appearance time method to PSM and NAIS data during particle formation events (see Section 3.2.2). The growth rate was found to equal 0.2 nm/h, 0.9 nm/h and 2.1 nm/h in the size ranges of <1.2 nm, 1.4–1.8 nm and 2–3 nm, which means that the growth rate increased with the increasing particle size. In addition, the particle growth rate expected due to irreversible condensation of sulfuric acid was estimated for the same three size ranges from measured sulfuric acid concentration (see Eq. (7) in Section 3.1.1). This growth rate was found to equal 0.3–0.4 nm/h, 0.6–0.9 nm/h and 0.5–0.6 nm/h in the size ranges of <1.2 nm, 1.4–1.8 nm and 2–3 nm.

By comparing the observed particle growth rates and the growth rates explained by condensation of sulfuric acid, three different size regimes can be recognized. In the first size regime (<1.2 nm), the observed growth was very slow and could easily be explained by the condensation of sulfuric acid. Therefore, the particles (or molecular clusters) in this size range likely take up and evaporate vapor molecules constantly and are not directly connected to particle formation events. This conclusion is also supported by the fact that particle concentrations in this size range were observed to be continuously high, also outside particle formation events. Previously it has been proposed that atmospheric neutral clusters are composed of sulfuric acid and some stabilizing compounds, such as ammonia (Kulmala et al., 2000). However, it is also possible that the very slowly growing clusters observed in this size regime consist mainly of organic molecules, and sulfuric acid is needed only in the next step, to enable the growth of clusters to larger sizes. The importance of organic compounds for the formation of the smallest particles in Hyytiälä is also indicated by the results from **Paper I** discussed in the previous section.

In the second size regime (~1.2–1.7 nm) the observed growth rate was slightly higher but it could still be explained by the condensation of sulfuric acid. The importance of sulfuric acid in this size range is suggested by the observed correlations between sulfuric acid and particle formation rates or particle concentrations (see Section 5.1.2). On the other hand, other compounds, such as amines, ammonia, or low-volatile organic vapors, are probably needed to stabilize the clusters, as theoretical results indicate that clusters containing only sulfuric acid (and water) cannot grow (Kurtén et al., 2008). The CI-APi-TOF measurements showed that amines and low-volatile organic compounds were indeed present in Hyytiälä during the measurement campaign.

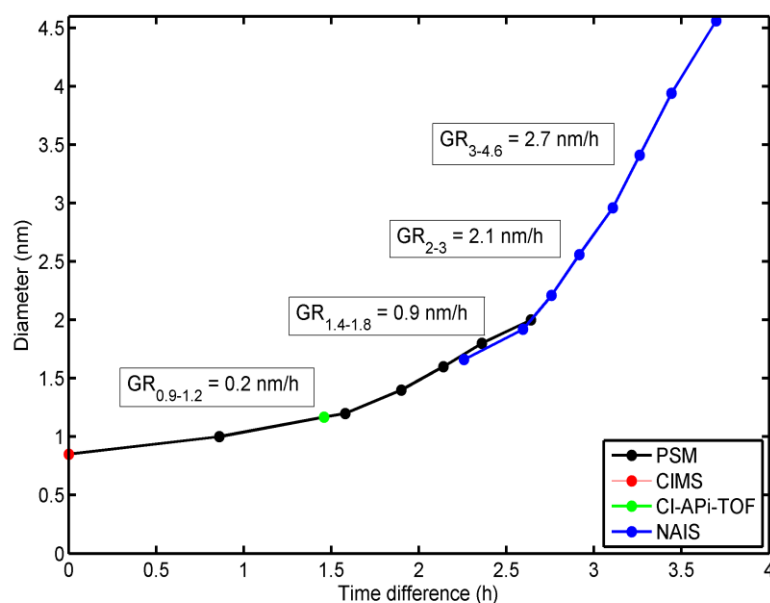


Figure 7. Particle size (in mobility diameter) as a function of time during particle formation events in Hyytiälä during spring 2011. Times when the concentrations reached half of their maximum were determined from different instruments: sulfuric acid concentration was determined from the CIMS, the concentration of an organic compound with a mass of 339.06 Th from the CI-API-TOF, and the concentrations of different-sized particles and ions from the PSM and the NAIS. Growth rates (GR) determined for different size ranges are shown in the figure. Figure adapted from **Paper I**.

In the third size regime (>1.7 nm) the observed growth rate was 2–4 times higher than the growth rate expected due to the condensation of sulfuric acid. This means that other compounds, most likely low-volatile organic vapors, are needed to grow the particles in this size regime. The enhanced growth can be caused, for instance, by nano-Köhler-type activation of clusters (Kulmala et al., 2004b), by heterogeneous nucleation of organic vapors, or by heterogeneous reactions between clusters and organic vapors (Wang et al., 2010). After clusters have been activated, their growth can accelerate further due to the decreasing Kelvin effect. The activation of clusters for the growth needs to take place so that a particle formation event with measurable values of the formation rate of 3-nm particles can be detected (see Section 5.1.1).

The accelerating growth of sub-3 nm particles has been observed in different environments ranging from a remote high-altitude site to a polluted Chinese megacity (Kuang et al., 2012b; Xiao et al., 2015; Bianchi et al., 2016). In addition, several earlier studies have reported that the particle growth rate increases with size in the 1.5–20 nm size range (e.g. Manninen et al., 2010; Yli-Juuti et al., 2011). Tröstl et al. (2016) studied the initial growth of particles caused by condensation of organic compounds utilizing measurements in the CLOUD chamber and a volatility distribution growth model. They concluded that the accelerating growth is mainly due to the decreasing Kelvin effect with the increasing particle size. At the smallest, sub-2 nm sizes only organic vapors with extremely low volatility

(ELVOCs) can participate in the growth but as the particles grow in size, abundant compounds with slightly higher volatility (LVOCs) are mainly responsible for the growth. Their results also indicate that CCN concentrations, predicted by a global aerosol model, are sensitive to whether, and if so how, organic compounds are assumed to participate in the growth of freshly-formed particles. In addition, Kuang et al. (2012b) showed that the size-dependency of the growth rate strongly affects the number of particles surviving to climatically relevant sizes, which demonstrates the importance of knowing the particle growth rate accurately in different size ranges.

5.2.2 Effect of acid–base clustering and ions on growth rate

It is challenging to quantify the role of different atmospheric constituents in particle growth solely based on field measurements. Therefore, a series of experiments was conducted in the CLOUD chamber to study the initial particle growth under well-controlled conditions using a wide range of instruments (**Paper V**). In part of the experiments, referred to as binary experiments, sulfuric acid and water vapor were added to the chamber, while other compounds were present only as impurities. In these experiments, ammonia concentration was most of the time below the detection limit (<35 pptv in CLOUD3 campaign and <5 pptv in CLOUD4 and CLOUD7 campaigns). In so-called ternary experiments, ammonia (about 100–1400 pptv) or dimethylamine (DMA; about 5–70 pptv) was added to the chamber to study their effect on particle growth. In addition, the effect of electric charge was investigated by comparing the experiments where ions were present in the chamber with the identical neutral experiments where ions were removed with a high-voltage clearing field.

The growth rates of particles in the 1.5–2.5 nm size range were determined from PSM data using the appearance time method (see Section 3.2.2). In Fig. 8 these growth rates are shown for different experiments as a function of the measured sulfuric acid concentration. The growth rate can be observed to increase almost linearly with the increasing sulfuric acid concentration at a certain ammonia or DMA concentration level. In the binary experiments, the observed growth rates were similar, or even lower, than the growth rates expected due to irreversible condensation of sulfuric acid, which were calculated using measured sulfuric acid concentration (see Eq. (7) in Section 3.1.1). In the ternary experiments, the particle growth was clearly enhanced compared to the binary case: the growth rate corresponding to a certain sulfuric acid concentration increased by a factor of 2–3 when >100 pptv ammonia was added to the chamber, and further by a factor of ~ 10 with the addition of >5 pptv DMA. The growth rates observed in the ternary experiments, especially in those involving DMA, clearly exceeded the growth rates explained by the condensation of sulfuric acid, even if co-condensation of bases was taken into account.

The explanation for the high growth rates observed in the DMA experiments can be found when studying the particle growth process at the molecular level. The measurements with the CI-APi-TOF show that when sulfuric acid and DMA are added to the CLOUD chamber, neutral clusters consisting of sulfuric acid and amine molecules with seemingly negligible evaporation rates are formed (Kürten et al., 2014). To investigate how these clusters can

affect the particle growth, cluster populations simulations were performed (see Section 3.3) and growth rates were determined from the simulated cluster size distributions using the similar method as for the measured data. If very low or zero evaporation rates were assumed for the clusters, the growth rates in the simulations were close to the growth rates observed in the DMA experiments (shaded area in Fig. 8). Thus, the enhanced growth of particles in the presence of DMA seems to be caused by reduced cluster evaporation rates as well as the contribution of small acid–base clusters to the growth. These sulfuric acid containing clusters are not observed if sulfuric acid concentration is measured with conventional chemical ionization mass spectrometer techniques allowing only the detection of sulfuric acid monomer (Eisele et al., 1993; Petäjä et al., 2009).

In the experiments where ammonia was added to the chamber, the growth rate did not increase as strongly compared to the binary case as in the DMA experiments. The CI-APi-TOF measurements indicate that in these experiments a smaller fraction of sulfuric acid was bound to acid–base clusters than in the DMA experiments. Therefore, the enhancement of growth observed while adding ammonia is likely mainly due to reduced evaporation rates caused by the stabilization effect of ammonia and the contribution of ammonia molecules to the cluster size.

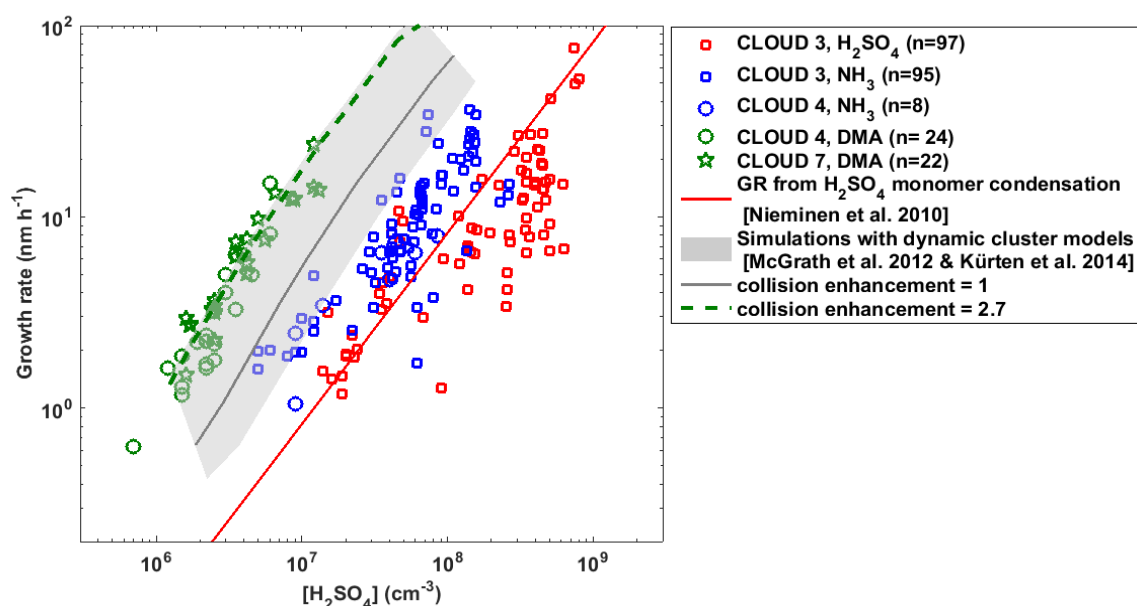


Figure 8. Growth rates of 1.5–2 nm particles as a function of measured sulfuric acid (H_2SO_4) concentration in the CLOUD chamber with different amounts of ammonia (NH_3) and dimethylamine (DMA). Red points refer to the experiments where ammonia was present only as an impurity, blue points to the experiments where ammonia was added to the chamber (100–1400 pptv), and green points to the experiments where DMA was added to the chamber (5–70 pptv). The red line shows the growth rates expected due to irreversible condensation of sulfuric acid. The gray line shows the growth rates determined from cluster population simulations assuming zero evaporation rates. A factor of 0.5–3 uncertainty was assumed for the cluster collision rates (represented by shaded gray area). The green dashed line shows the growth rates corresponding to a collision enhancement factor of 2.7. Figure adapted from **Paper V**.

According to theoretical studies, the presence of electric charge can enhance particle growth by increasing the collision rates of polar vapors on charged clusters or by decreasing the evaporation rates of charged clusters (Laakso et al., 2003; Nadykto and Yu, 2003). The CLOUD experiments enabled to determine the magnitude of this enhancement for the first time experimentally. The growth enhancement factor was determined by calculating the ratio of the particle growth rate obtained in the presence of ions to the growth rate obtained in the corresponding neutral conditions. In the binary sulfuric acid–water system, the growth enhancement factor was found to be on average about 3 at 1.5 nm and about 2 at 2 nm. These values are consistent with theoretical predictions on the growth enhancement caused by increased collision rates (Laakso et al., 2003; Nadykto and Yu, 2003), although the observed growth enhancement may also be caused by the stabilization effect of ions. When ammonia was added to the chamber, the growth enhancement factor was found to decrease slightly compared to the binary case. However, in the DMA experiments, the growth enhancement factor was close to unity at both sizes, meaning that the presence of ions did not significantly enhance the particle growth in this case. This may result from the fact that in the DMA experiments particle formation proceeds mainly by neutral mechanisms, and thus the increase in collision rates has a negligible effect on growth rate, or then the reason is that DMA is able to stabilize the clusters so effectively that in its presence further stabilization by ions is not needed. These results imply that the growth enhancement of ions may be important in very clean environments, such as in the free troposphere, whereas in the planetary boundary, where stabilizing compounds are usually available, this effect is likely only minor.

Overall, these results from the CLOUD experiments indicate that the initial growth of atmospheric particles in the presence of sulfuric acid, water, ammonia or amines, and ions is driven by sulfuric acid. In the conditions with low concentrations of stabilizing compounds, the growth proceeds by monomer additions and is assisted by ions. In the presence of stabilizing compounds, the growth is enhanced and cluster–cluster collisions can also contribute to the growth. In **Paper VI**, the effect of cluster–cluster collisions on the growth of a cluster population was further studied by utilizing cluster population simulations. The simulation results show that cluster–cluster collisions can significantly contribute to the growth if cluster concentrations are high. This corresponds to the conditions with low saturation vapor pressure (and thus low evaporation rates), high monomer source rate, and low external losses. Figure 9a illustrates the effect of saturation vapor pressure on the non-monomer fraction of particle fluxes, showing how the contribution of cluster–cluster collisions increases with decreasing saturation vapor pressure. Furthermore, in one simulation set a situation with elevated concentrations of stabilized small clusters was studied by assuming a different Gibbs free energy profile than in other simulations (see Section 3.3). In this case the growth was observed to proceed mainly by cluster–cluster collisions. This further demonstrates that when investigating particle growth experimentally or theoretically, the time development of the full cluster size distribution should be taken into account.

5.2.3 Comparison of different growth rate methods

When studying particle growth mechanisms, growth rates determined using different methods are often compared with each other. This is also done in this thesis in **Papers II** and **V**, where the growth rates determined from the appearance times of different-sized particles (AGR; see Eq. (8)) are compared with the growth rates caused by irreversible condensation of vapor (CGR; see Eq. (7)). However, it is unclear how consistent different growth rate methods are. Therefore, in **Paper VI** growth rates determined with different methods were compared with each other using cluster population simulations. In addition to AGR and CGR, the growth rate corresponding to the flux between adjacent size bins (FGR; see Eq. (6)) was studied. The relation between different growth rates was studied in different conditions by varying the saturation vapor pressure of the model substance (to which evaporation rates are directly proportional), the vapor monomer source rate and the magnitude of the external sink. In addition, a set of simulations was performed with elevated concentrations of stabilized small clusters.

Figure 9 illustrates the different growth rates in one of the simulation sets, where saturation vapor pressure of the model substance was varied. In the majority of the simulations FGR was observed to be lower than AGR or CGR. The difference was highest, often several orders of magnitude, in the smallest size bin (at ~ 1.2 nm in mass diameter), while in the largest size bin (at ~ 2.2 nm in mass diameter), FGR was closer to AGR and CGR (see Fig. 9e). The difference between the growth rates generally decreased when cluster concentrations were high, and thus evaporation and other losses less important, i.e. in the conditions with low saturation vapor pressure, high monomer source rate and low external losses. In the simulation set with the elevated concentrations of stable small clusters, FGR was observed to be closer to AGR and CGR than in other simulations. In addition, when using a better size resolution, meaning that the size bins were narrower, FGR was observed to become closer to AGR and CGR. When studying how FGR is calculated, one can observe that too low values of FGR result from the approximation made in its derivation: the flux from the size bin is divided by the mean value of the size distribution function in that bin ($N_i / \Delta D_{p,i}$ in Eq. (6)), while, theoretically, it should be divided by the value at the bin boundary (Vuollekoski et al., 2012). This approximation affects the obtained growth rate most dramatically in the smallest size bin, where the concentration decreases fast with the increasing size. For this same reason, if particle formation rates are calculated utilizing particle growth rates according to Eq. (4), the resulting values may be too high.

Although large differences between FGR and other growth rate definitions were observed, AGR and CGR were found to be rather close to each other: their difference was often very small (see Fig. 9f) and within the factor of 10 in all the simulations. This can be considered as a slightly unexpected result, as AGR is affected by all possible collision and evaporation processes, while CGR is derived considering only the condensation of single molecules. Still, when determining growth rates from experimental data for nanometer-sized particles, it should be kept in mind that different approaches may result in different values of growth rates depending on the ambient conditions, the properties of the condensing vapor and the size resolution used in the analysis.

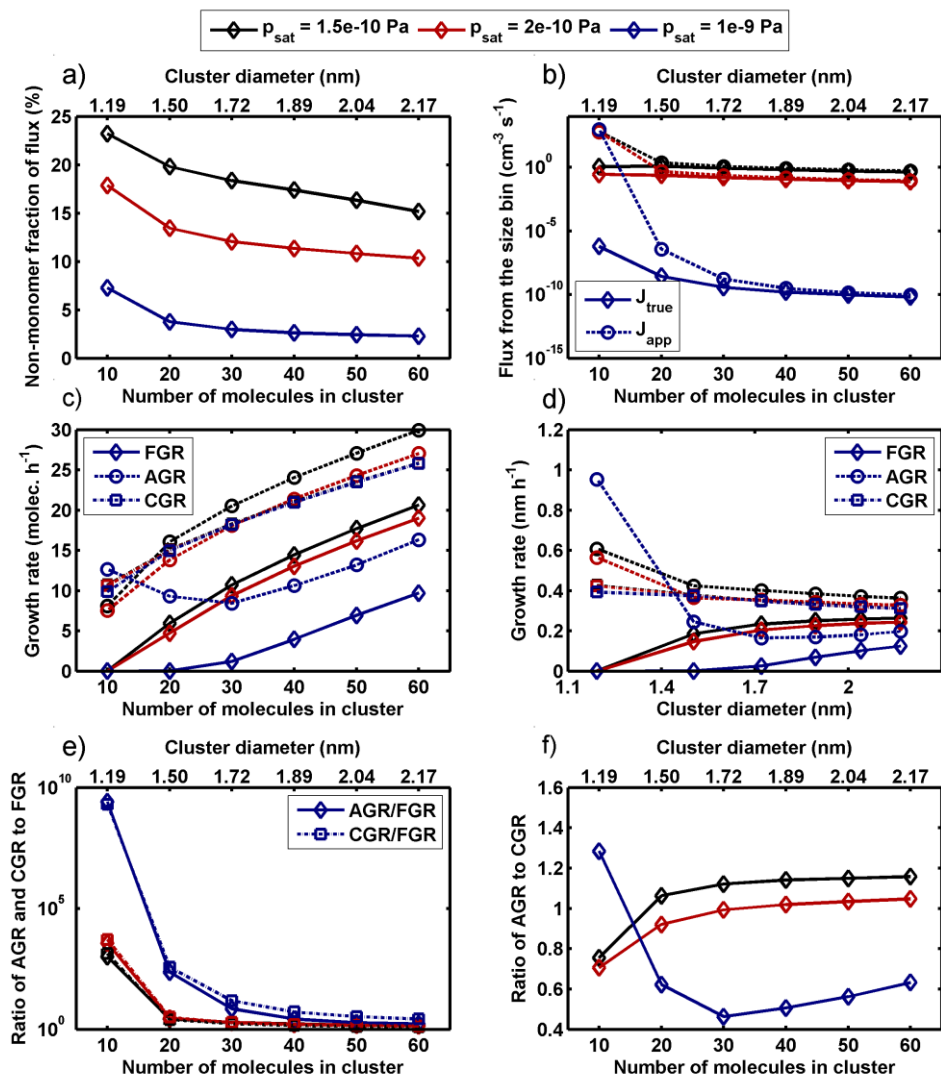


Figure 9. The effect of saturation vapor pressure (shown as different colors) on quantities describing cluster growth in cluster population simulations: a) the non-monomer fraction of flux from each size bin, b) the true collision-evaporation flux from each size bin (J_{true} ; solid line) and the fluxes calculated from the appearance times of clusters (J_{app} ; dashed line), c) and d) the flux-equivalent growth rate (FGR; solid line), the growth rate derived from the appearance times of clusters (AGR; dashed line), and the growth rate calculated based on irreversible vapor condensation (CGR; dotted line), e) the ratios of AGR to FGR (solid line) and CGR to FGR (dotted line), f) the ratio of AGR to CGR. Figure adapted from **Paper VI**.

6 Review of papers and the author's contribution

Paper I presents the comparison of the concentrations of sub-3 nm atmospheric particles measured with a PSM at nine sites around the world. Sub-3 nm particle concentrations were observed to be highest at the sites with strong anthropogenic influence. In boreal forest, sub-3 nm particle concentration was higher in summer than in winter, indicating the importance of biogenic precursor vapors. At all the study sites particle concentrations were higher during daytime than at night. When comparing the total sub-3 nm particle concentrations to ion concentrations, electrically neutral particles were found to dominate in polluted environments and in boreal forest during spring and summer. In this paper, I performed the data analysis and wrote most of the text.

In **Paper II** the first steps of atmospheric particle formation were investigated utilizing the measurements of sub-2 nm neutral and charged particles and their precursor vapors conducted at a boreal forest site in Hyytiälä, Finland, during spring 2011. Based on the analysis of particle formation and growth rates, three different size regimes related to particle formation were identified. Neutral pathways were found to dominate particle formation. The results also suggest the importance of organic compounds in accelerating the initial particle growth. In this paper, I performed a major part of the data analysis and contributed to writing of the paper.

Paper III introduces a novel method for estimating the contribution of ion-ion recombination to sub-3 nm particle concentrations. In this method the production of recombination products in collisions between oppositely charged ions, the loss due to coagulation, and the effect of condensational growth are considered. The method was applied to the data measured in Hyytiälä during spring 2011. The recombination products were found to only account for a minor fraction of all neutral sub-2 nm particles. In this paper, I performed the data analysis and wrote most of the text.

Paper IV presents the observations of neutral and charged sub-3 nm particles and their connection to new particle formation in San Pietro Capofiume, Italy, during summer 2012. A high number of sub-3 nm particles was detected and the majority of them were found to be electrically neutral. The dynamics of sub-3 nm particles during particle formation events was concluded to be rather similar as in boreal forest, although particle formation rates were higher. In this paper, I participated in the data analysis and wrote most of the text.

In **Paper V** the effect of acid-base clustering and ions on the growth of sub-3 nm particles was studied based on the comprehensive measurements conducted in the CLOUD chamber. Cluster population simulations were also utilized to study the growth mechanism. The results of the paper show that small acid-base clusters and ions can enhance the initial particle growth rates. The magnitudes of these enhancements depend on the concentrations of base compounds. In this paper, I performed the cluster population simulations and contributed to the writing of the paper.

In **Paper VI** the consistency of the growth rates determined for sub-3 nm particles using different methods was investigated using cluster population simulations. It was observed that different methods may give different values for the growth rates depending on the ambient conditions, the properties of the condensing vapor, and the size resolution used in the analysis. The differences were generally largest at the smallest, sub-2 nm sizes and in the conditions where evaporation and other losses were significant. In this paper, I performed the simulations and the data analysis, and wrote most of the text.

7 Conclusions and outlook

New particle formation has been observed to occur frequently in various environments around the world (Kulmala et al., 2004a). It produces most of the aerosol particles in the atmosphere and even half of the CCNs (Spracklen et al., 2006; Merikanto et al., 2009). Despite extensive research on particle formation mechanisms during recent years, many fundamental questions remain open. This is because the first steps of particle formation and growth occur in the region between nanometer-sized molecules, molecular clusters, and particles, which makes measuring and modeling of the processes challenging. The aim of this thesis was to elucidate some of the unresolved issues related to atmospheric particle formation by investigating the dynamics of sub-3 nm atmospheric particles.

The first objective (*i*) of this thesis was to develop and evaluate theoretical methods to study the dynamics of sub-3 nm particles. The analysis of measurements conducted with novel instruments, especially with a PSM, forms the core of this thesis. Particle formation rates and growth rates were determined from PSM data by applying earlier developed methods to new data sets but also by utilizing new methods (**Papers II, IV and V**). The role of ion-mediated mechanisms in particle formation was investigated by developing a novel method to determine the size-distribution of recombination products from measured data (**Paper III**). In addition, cluster population simulations were used to study the initial growth mechanism (**Paper V**) and to assess the consistency of different methods to determine particle growth rates (**Paper VI**).

The second objective (*ii*) was to provide a comprehensive picture of the concentrations and dynamics of sub-3 nm atmospheric particles in different environments. This objective was fulfilled by analyzing PSM measurements from several measurement sites around the world (**Papers I, II, and IV**). The 1–3 nm particle concentrations were observed to be highest in polluted environments, such as in Chinese megacities, which indicates the importance of anthropogenic sources of low-volatile precursor vapors. On the other hand, in boreal forest sub-3 nm particle concentration was clearly higher in summer than in winter, suggesting that biogenic precursor vapors are important in forested regions. Sub-3 nm particle concentration was observed to be highest during daytime, which is likely linked to the photochemical production of precursor vapors. When comparing ion concentrations measured with an ion mobility spectrometer to the total sub-3 nm particle concentrations, electrically neutral particles were observed to dominate in polluted environments and in boreal forest during spring and summer. Finally, the results also suggest that the concentrations of sub-3 nm particles are determined by the availability of precursor vapors rather than the value of the sink due to pre-existing aerosol particles.

The third objective (*iii*) was to increase the understanding of the first steps of atmospheric particle formation and growth and the role of neutral and charged particles and different gaseous compounds in these processes. This objective was fulfilled by analyzing comprehensive measurements of sub-3 nm neutral and charged particles and their precursor vapors conducted in the field (**Papers I–IV**) and in the laboratory (**Paper V**). The results indicate that the formation of clusters and their further growth are two separate processes. Small sub-2 nm clusters seem to be formed continuously in the atmosphere but their growth to 3 nm occurs only if the conditions

are favorable, in which case a particle formation event is observed. Particle formation is likely dominated by neutral pathways, while ion-induced nucleation and ion-ion recombination have only a minor contribution. Sulfuric acid seems to be important in particle formation, although in boreal forest low-volatility organic compounds are likely also significant. The particle growth rate accelerates with the increasing particle size in the sub-3 nm size range. The enhancement of the growth is probably caused by low-volatile organic vapors, at least in boreal forest. On the other hand, in the system containing sulfuric acid, amines or ammonia, and ions, acid-base clusters and ions can enhance the growth, and the magnitudes of the enhancements depend on the availability of base compounds.

Overall, it can be concluded that this thesis has improved the understanding of the dynamics of atmospheric sub-3 nm molecular clusters and particles, especially related to the first steps of particle formation and growth (see Fig. 10). This knowledge is essential when estimating how aerosol formation affects the climate by modifying cloud properties, both in the present day and in the future. Although some studies utilizing global aerosol models suggest that CCN concentrations are rather insensitive to initial particle formation rates (Pierce and Adams, 2009; Lee et al., 2011; Westervelt et al., 2014), others indicate that to accurately predict global CCN concentrations, the detailed understanding of particle formation and growth mechanisms, especially related to the role of organic compounds, is needed (Riipinen et al., 2011; Tröstl et al., 2016). In addition, the understanding of the chemical and physical processes of aerosol formation is important when solving severe air quality problems faced in polluted urban areas (Kulmala, 2015). For instance, secondary aerosol formation has been observed to significantly contribute to particulate pollution events in Chinese megacities (Huang et al., 2014).

Despite the advancements in understanding atmospheric particle formation resulting from this thesis, many issues remain to be resolved. It is probable that different mechanisms govern particle formation and growth in different environments. For example, a recent study showed that in coastal areas particle formation can be dominated by iodine oxide vapors (Sipilä et al., 2016), while in other regions, such as in forests or polluted megacities, the compounds participating in the process are likely completely different. Therefore, size-segregated measurements of sub-3 nm neutral and charged particles and molecular clusters should be conducted in different environments ranging from extremely clean sites to highly polluted regions. Especially, measurements should be performed on the Southern Hemisphere and remote marine and polar regions where measurements have so far been scarce. In addition, instrumental development is essential to ensure the reliability of the measured concentrations, and to characterize the composition of detected particles. The development of mass spectrometry techniques is needed to measure the concentrations of gaseous compounds participating in particle formation, including different organic vapors but also base compounds such as ammonia and amines. Finally, modeling of particle formation and growth on different scales from the behavior of nanometer-sized clusters to the global climate system is also needed to understand the processes and their effects on the climate and air quality.

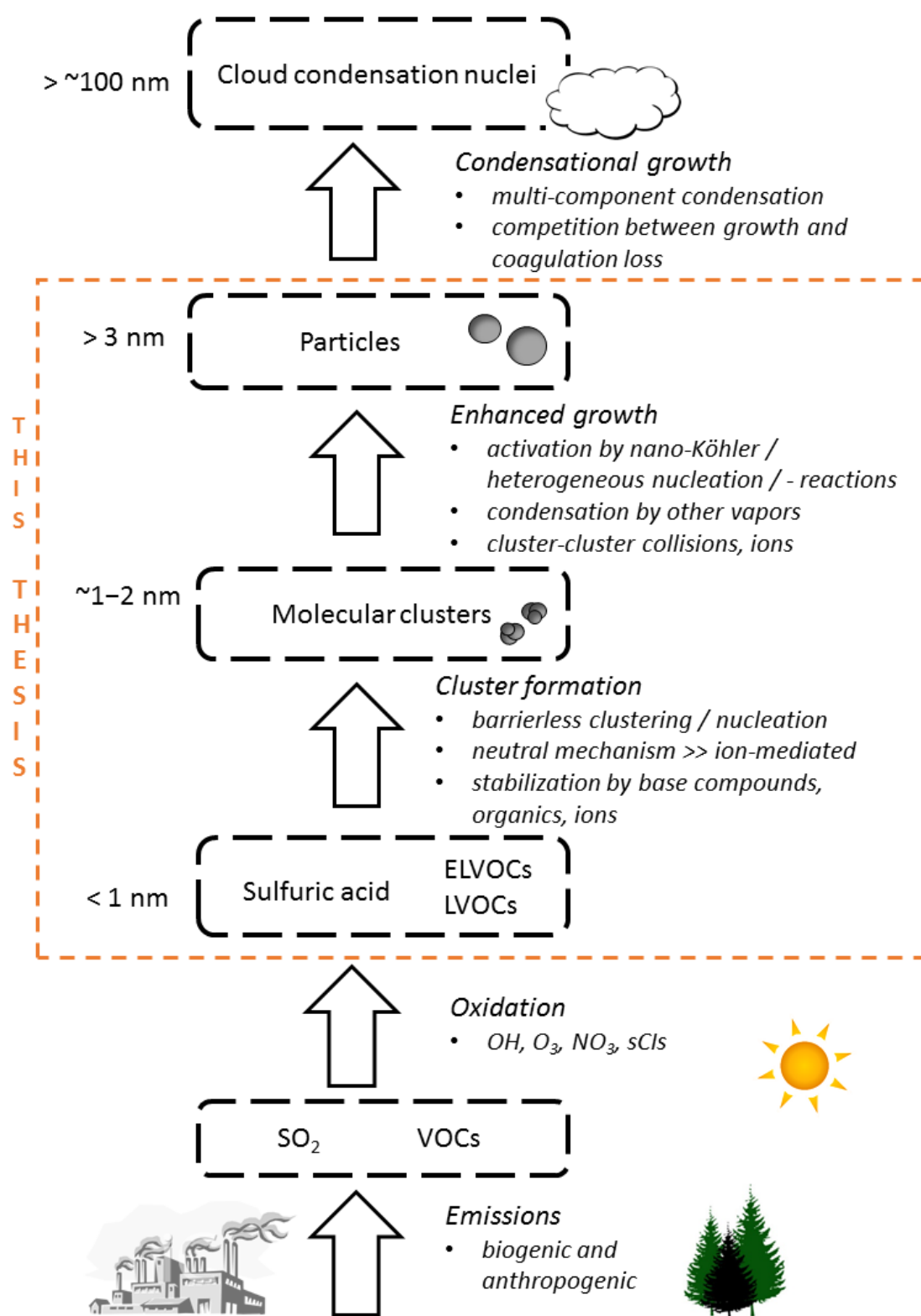


Figure 10. The schematic figure illustrating the current understanding of atmospheric particle formation based on the results of this thesis. The orange box shows the focus area of the thesis.

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